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OLUME 30, No. 24

AMERICAN

DYESTUFF REPORTER

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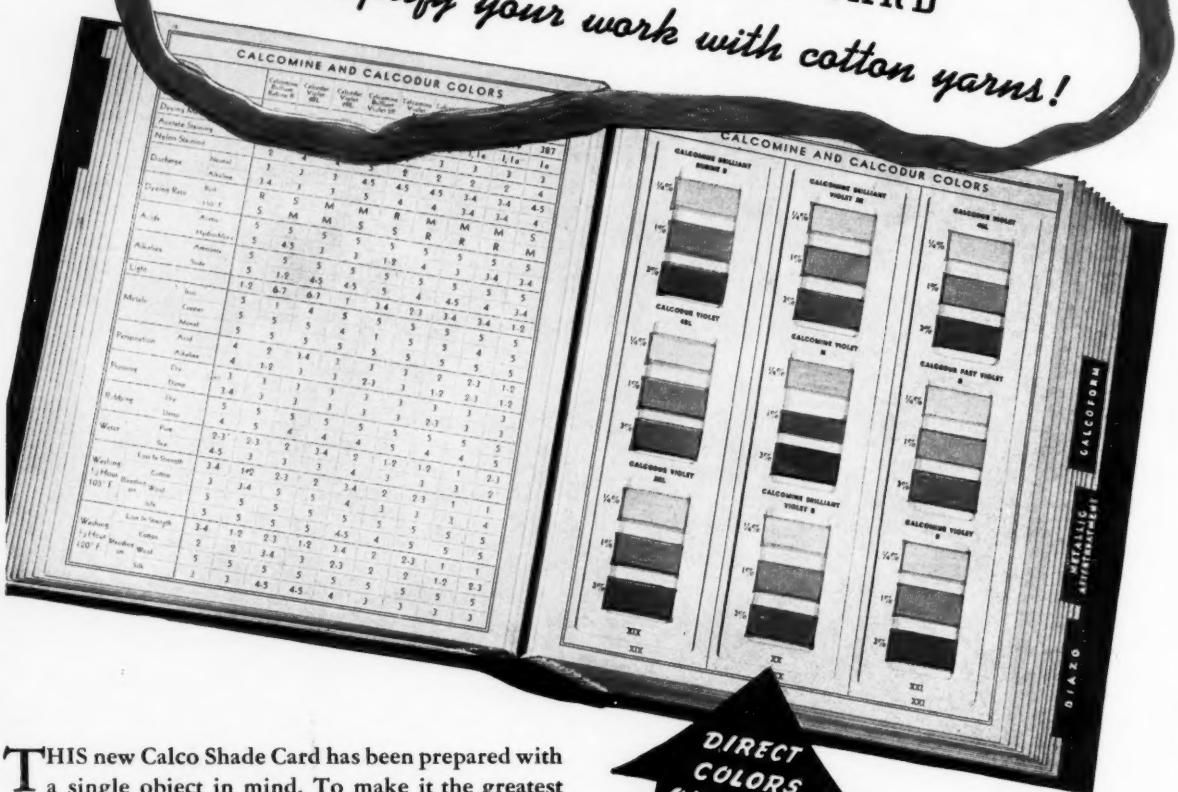

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DYESTUFF REPORTER

VOLUME 30 NOVEMBER 24, 1941 NUMBER 24

A Study of GAS FADING of Acetate Rayon Dyes

FRANK P. GREENSPAN* and PAUL E. SPOERRI**

INTRODUCTION

FOR almost a decade, and with increasing occurrence, a puzzling type of fading phenomenon has been encountered with acetate rayon dyes. Blue, green, violet, and the mode shades of acetate rayon fabrics stored away on shelves or in use have been mysteriously faded. This fading, known as gas fading (sometimes called atmospheric fading) is marked by a definite and characteristic reddening of the fabric, now known to be caused by the action of certain gaseous constituents of the atmosphere, notably "oxides of nitrogen."

Goodall[1] showed that blue acetate rayon fabrics were susceptible to a fading taking place in the dark, reproduceable by burnt gas fumes, and caused by the presence therein of nitrogen oxides. The same dyes were found to be sensitive to acids, which could be demonstrated by exposure to SO_2. While fadings resulting from the latter were restored to their original colors by ammonia, those resulting from exposure to "oxides of nitrogen" were permanent. Rowe and Chamberlain[2] demonstrated that whereas burnt coal gas fumes were capable of causing gas fading, the same gas, stripped of its "oxides of nitrogen" by absorption in a special chromic acid reagent, no longer caused fading. Furthermore, similar fadings could be obtained with "oxides of nitrogen," generated by the acidification of sodium nitrite, with sulfur dioxide exerting a modifying influence on this action. When these "oxides of nitrogen" were aspirated through water suspensions of different aminoanthraquinone dyes (the most sensitive series of acetate rayon dyes), the same authors reported evidence of diazotization with dyes containing a primary amino group and nitrosoamine formation with those having a secondary amino group.

Recent years have seen the development of anti-fume finishes designed to inhibit gas-fading. While some anti-fume finishes have been developed which successfully inhibit gas fading, the "A.A.T.C.C. Committee on Atmospheric Fading of Dyed Acetate Rayon" reports[3] that anti-fume finishes "cannot be considered as solving the fading problem." It is the judgment of this committee that the gas fading problem will be solved satisfactorily only by the production of new acetate rayon dyes resistant to gas fumes.

Such a synthesis implies a recognition of the factors and mechanism of the fading process. It has therefore been considered worthwhile to attempt a rigorous study of gas fading with particular emphasis on the factors influencing the action of "oxides of nitrogen" on the aminoanthraquinones and to attempt a study of the reactions involved therein.

EXPERIMENTAL

A. Exposure Of 1:4 Diaminoanthraquinone Dyed Fabrics to Nitrogen Oxides

"Oxides of nitrogen" are normally present in the atmosphere to the extent of 1-2 parts per 100 million by volume according to Francis & Parsons[4] and in a fog or smoky atmosphere[5] may rise to 15-16 parts. Wood and Davey[6] report that the "oxides of nitrogen" content in the undiluted products of coal gas combustion is 1-2 parts per 100,000 by volume calculated as NO.

The presence of "oxides of nitrogen" in the atmosphere results from the combustion of gases and fuels, and this oxidation of nitrogen is a minor arc process taking place in the intense heat of a combustion. While NO is normally regarded as the first product of combustion of N_2[7, 8] (NO is slowly oxidized further to N_2O_4) and can be produced by drawing N_2 and O_2 over a hot gaseous flame [9, 10], N_2O has also been found as a combustion product of N_2[7, 8, 11].

Experimental methods heretofore employed for duplicating gas fading in the laboratory have used impure mixtures of oxides of nitrogen obtained from (1) burnt coal gas fumes, and containing, as used, all the products of combustion of nitrogen (NO, N_2O_3, N_2O_4, and possibly

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N_2O) or (2) acidification of nitrite yielding a mixture (NO, N_2O_3, N_2O_4). It has therefore been deemed advisable to study the action of pure individual nitrogen oxides as a step to the clarification of the term, "oxides of nitrogen." A series of tests were conducted with 1:4 diaminoanthraquinone, a sensitive violet acetate rayon dye, and the new A.A.T.C.C. control for gas fading, Celanthrene Brilliant Blue FFS, in which dyeings of the above were exposed to pure atmospheres of these gases over an extended period of time.

Experimental dyeings were made with an acetate rayon taffeta of standard construction, using 1/10 per cent pure 1:4 diaminoanthraquinone (prepared by purification of the commercial dye) for light shades and 6/10 per cent for heavier shades based upon dry fabric weight, a bath to fabric ratio of 40:1 being employed. Prior to dyeing, the grey goods were scoured in a standard type acetate rayon scouring bath. The dye was dispersed with the aid of a soap solution (total soap = 4 per cent of the weight of acetate rayon), made up to the proper volume, and the scoured grey goods introduced at 120° F, raised slowly to 180-200° F., and treated at that temperature for approximately 45 minutes with continuous stirring until proper penetration and exhaustion. After rinsing, the dyed fabric was air dried.

The Celanthrene Brilliant Blue FFS used was the acetate rayon satin designated as a control sample for gas fading test work by the A.A.T.C.C.[12].

I. Action of Nitrous Oxide (N_2O) On Dyeings

Small samples of the 1:4 diaminoanthraquinone light dyed taffeta were placed in Schwarz type U-tubes with side arms and glass stopcocks. Nitrous oxide from a tank source (free of NO and N_2O_4) was connected to the exposure tubes, and a stream of the gas passed through for 30 minutes, at the end of which time, with the gas stream turned off, the stopcocks were closed, and the tops of the cocks sealed with a lacquer. The tubes were then kept in the ordinary light of the room, a blank being maintained in a similar tube for comparison purposes. No color change could be observed at the end of the N_2O passage, nor at the end of two months of periodic examination.

Samples of the Celanthrene Brilliant Blue FFS dyed acetate rayon satin exposed to a N_2O atmosphere in similar fashion likewise showed no change in color when compared with a blank.

*II. Action of Nitric Oxide (NO) on Dyeings**

Preliminary experiments revealed that a pure controllable stream of NO could be obtained by the action of 1:1 H_2SO_4 on a mixture of one part of KI to two parts of KNO_2 dissolved in distilled water[13]. Both the water and acid were freshly boiled to remove dissolved air.

A suitable apparatus, completely air free, and providing sufficient flexibility to allow for the attachment of exposure tubes containing sample dyeings and their removal at the end of the gas passage without admission of air, was developed after considerable work and constant revision. The apparatus is illustrated in Diagram I. Rubber stoppered wash bottles were found most satisfactory. All joints and rubber tubing connections (glass to glass) were sealed with a double coat of lacquer. The entire apparatus was tested for leaks by checking on the synchronization of the gas bubbles in the various bottles when a very slow periodic stream of N_2 was passed through.

To guard against the formation of minute amounts of N_2O_4† resulting from air leaks or sealing operations, special type exposure tubes, Diagram II, designed for attachment to the NO apparatus after the insertion of a sample dyeing, were used. These were made by taking Schwarz U-tubes with soda-lime in the side arms and sealing these arms to tubing that entered directly into the H_2SO_4 bottles on both sides of the exposure tube, the tubing being constricted as indicated for sealing purposes.

In use, exposure tubes containing sample dyeings, were attached at Section II, Diagram I, and a N_2 stream swept through the apparatus for 45 minutes. During the last 15 minutes of the N_2 passage, the NO generation was begun with two-way stopcock, M, open to the air. The N_2 stream was then cut, stopcock M switched to the system, and a uniform stream of NO passed through the apparatus for 30 minutes and observation made of any color change by comparison with a blank (an analagous dyeing sealed in air in a like exposure tube). With the conclusion of a ½ hour passage of NO, the cocks of the exposure tubes were closed, 2 way stopcock, M, opened to the air, the tubes sealed at the constrictions with a microburner and the cocks lacquered. The sealed tubes now contained an aminoanthraquinone dyed acetate rayon in a pure NO atmosphere and were allowed to stand in the ordinary light of the room, periodically being compared with a blank. The following observations were made:

Sample:1:4 diaminoanthraquinone dyed taffeta—dark shade violet. (1) For approximately 20 minutes of NO passage—no observable fading. (2) At the end of 30 minutes—slight redness—not very noticeable alone, but definite when compared with blank. (3) At the end of 2-day period—redness increased—now red violet. (4) At the end of 1 week—light red toward pink in color.

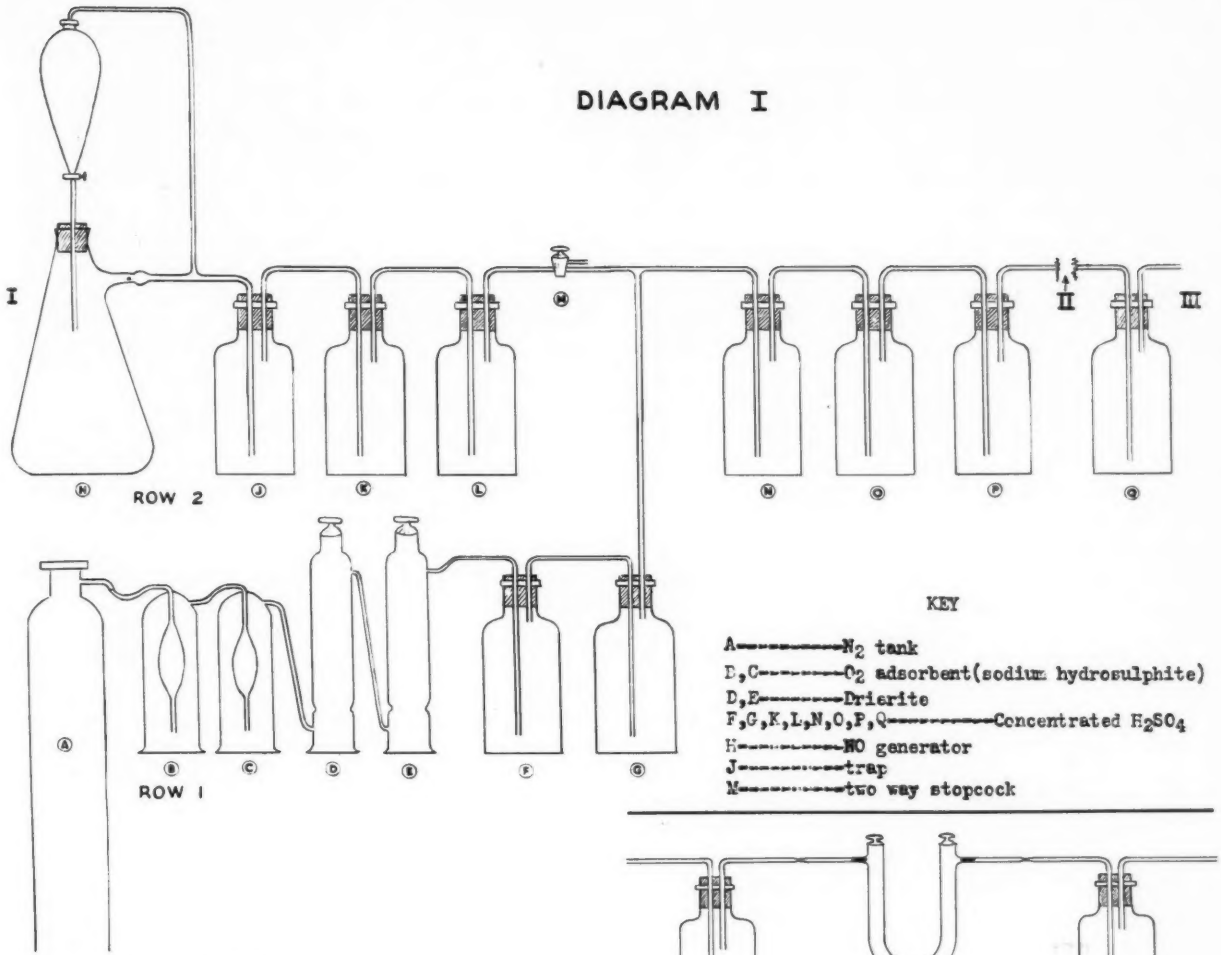
The color changes were strikingly similar to the actual gas fadings encountered with 1:4 diaminoanthraquinone and other dyes. Several samples were maintained in the tubes for 5 month periods with progressive lightening of the red and the development of a light orange-red color.

When tests were conducted with light shades of 1:4 diaminoanthraquinone dyeings (1/10 per cent), similar results were observed through with a definitely greater rapidity.

*Although NO as such would not exist for long in the atmosphere, it is present in the gases heretofore used for experimentally duplicating gas fading, and is a possible reduction product of the higher nitrogen oxides.

†It was already known that exposure to N_2O_4 caused rapid and severe fading.

DIAGRAM I



(1) At the end of 30 minutes—slight redness.

(2) At the end of 3 days—pink.

In contrast, fadings were more difficult to observe with deeper colors during the first 2 days of exposure.

Sample:—Celanthrene Brilliant Blue FFS dyed satin.

(1) At the end of 30 minutes—lighter blue.

(2) At the end of a 2-day period—reddening and lightening of blue color, strikingly similar to the "standard of fading" developed by the A.A.T.C.C. for use in testing apparatus with this dye.

(3) The color develops a greater reddishness with time and after a few months loses its blue identity, becoming dusty pink.

A blank tube (Diagram II), exposed to a N_2 and then a NO passage in duplication of the procedure used with sample dyeings, and then sealed, was examined spectroscopically after one month standing. No adsorption bands for N_2O_4 could be detected, thus establishing the purity of the NO used.

Further, using a Schwartz type U-tube, a sample 1:4 diaminoanthraquinone dyeing was inserted on the bottom. A wad of cotton was placed on top of the dyeing (not direct contact) and soda lime added above the cotton in both arms of the tube. The fabric was thereby fully

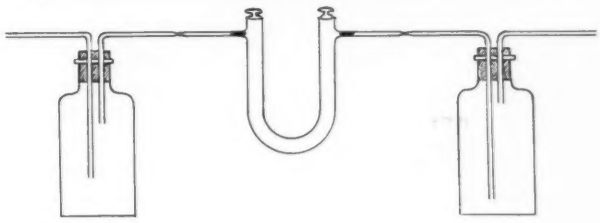


DIAGRAM II
EXPOSURE TUBE

protected from any possible N_2O_4, since it was surrounded by a N_2O_4 adsorbent. Runs conducted with these tubes showed the same reddening action of the gas, though clearly more slowly than without the soda lime (attributable to the desiccating action of soda lime and the slow reaction of NO with soda lime to give N_2O.)

Since acetate rayon has a normal regain of about 6.5 per cent at 65 per cent relative humidity and 70° F, and in view of the known hydrolysis of NO with water to yield HNO_2,[14] it was deemed important to discover the action on NO on 1:4 diaminoanthraquinone dyed fabrics dried so that no moisture was present.

Samples of dyeings were dried in an oven at 105°-110° C. for 1½ hours and then directly inserted into the exposure tubes brought up to the oven. With the U-tube resting in an oil bath maintained at 110°-125° C. so that the fabric was heated, a stream of N_2 was passed through

for 1½ hours. The bath was then removed and the dry N_2 stream maintained an additional 30 minutes, when the NO stream flowing through M into the air was switched to the system. A 30 minute NO passage followed, the procedure being the same as that previously described.

Sample :—1 :4 diaminoanthraquinone dyeing (1/10%).

(1) At end of 30 minutes—very slight reddening—comparison with blank (also dried at 105°-110° C.) necessary to note change in color.

(2) 2 days later—definite increased redness.

(3) 10 days later—red.

In all cases, the fading action during the first few days with dried samples was slower and more difficult to observe than with samples containing moisture. Observed over a period of two months, a light red color was maintained by the dried samples in contrast to the progressive fading with the acquirement of orange tinting observed with those samples having a moisture regain.

Effect of Heat on NO Action

A sealed exposure tube containing a 1 :4 diaminoanthraquinone dyeing in an NO atmosphere (prepared the previous day) was placed in an oven at 105°-110° C. Within a few minutes, the reddish-violet dyeing turned yellow (N_2O_4 also produces a yellow color). A similar tube having a dried acetate rayon sample in NO, maintained its reddish violet color without change, even after prolonged heating at the same temperature.

Effect of Light on NO Action

Light has been claimed to have no inuflence on gas fading[2]. Initial experiments with 1 :4 diaminoanthraquinone dyeings indicated a lesser degree of fading when NO exposures were conducted in dark tubes.

Exposure tubes, Diagram II, were lacquered on one arm only, and then samples of a 1 :4 diaminoanthraquinone dyeing were inserted into the tube, one into each arm. Thus, both a light and dark experiment could be conducted simultaneously in the same atmosphere under duplicate conditions. At the end of a week, the lacquer was removed from the dark tubes. Both tubes had definitely faded to red, but the "dark experiment" dyeings retained more blue than the light exposed ones, appearing reddish violet in contrast to the pink of the light exposed.

III. Action of Nitrogen Tetroxide (N_2O_4) On 1 :4 Diaminoanthraquinone Dyeings

N_2O_4, generated by the action of concentrated HNO_3 on Cu, was aspirated through successive towers of Drierite after previous passage through a layer of Cu turnings to remove any HNO_3 spray, and then through a 1 :4 diaminoanthraquinone dyeing (violet) contained in exposure tubes as heretofore.

A rapid and destructive action was observed with the standard dyeings—the violet almost immediately turning red and then yellow. With continued N_2O_4 passage, an almost bleached white could be obtained.

When the 1 :4 diaminoanthraquinone dyed acetate fabric was dried (as in the procedure outlined under NO action), the same rapid almost instantaneous action was noted.

Passage of N_2O_4 through black lacquered tubes produced identical results with those obtained on light exposed tubes.

B. Exposure of Undyed Cellulose Acetate to N_2O_4

Samples of undyed scoured acetate rayon and cellulose acetate crumbs were exposed to a rapid stream of N_2O_4, generated as above. At the end of a 30 minute exposure, the rayon had acquired a yellow color and was severely attacked in spots which were leathery and visibly altered in appearance.

A sample of freshly exposed acetate rayon was washed well with warm distilled water, treated in a warm concentrated urea solution for several hours to remove nitrous acid adsorbed, and then washed and air dried.

Treated with diphenylamine reagent, a blue coloration was obtained, not obtainable with a blank acetate rayon sample, and indicating the presence of cellulose nitrate. Part of the urea treated rayon was hydrolyzed with 5 per cent NaOH for several minutes, filtered, and drops of the resultant filtrate added down the sides of a test tube containing one ml. of diphenylamine reagent.[15] The characteristic blue ring at the zone of contact indicated a nitrate, oxidizing agents and nitrous acid being absent.

To test for free acetic acid, a sample of the severely exposed cellulose acetate was shaken with warm distilled water, allowed to stand a short time, filtered, made alkaline by addition of a few drops of ammonia, and concentrated by evaporation to a few ml. One drop of this solution was added to a spot plate and acetic acid tested for by the addition to this of one drop of a 5 per cent lanthanum nitrate solution, a drop of 0.02 N alcoholic iodine solution, and a few drops of dilute ammonia. On standing a short while, a faint blue-violet color, characteristic of acetic acid was obtained, not obtainable with a blank.

Samples of acetate rayon exposed to N_2O_4 under less severe conditions (a slower stream for 15 minutes) acquired a yellowish color but gave negative tests for nitrate and acetic acid.

The action of "N_2O_4 exposed" undyed acetate rayon on 1 :4 diaminoanthraquinone was investigated to check on the possibility that an intermediate substance formed by the action of N_2O_4 on acetate rayon caused the fading, rather than the direct action of N_2O_4 on the dye.

Samples of cellulose acetate crumbs, exposed to a 15 minute passage of N_2O_4 followed by N_2, and evacuated in a side arm flask to 5-10 m.m. for 3 hours, when added to a blue benzene solution (1/10 per cent) of Celliton Fast Blue AF (an aminoanthraquinone dye) caused the dye solution to become pink. A blank had no effect on the same. Similarly treated cellulose acetate crumbs gave a faint pink when tested with the sensitive napthylamine-sulfanilic acid reagent (test for nitrous acid). A blank of cellulose acetate developed almost a like intensity of pink (reagent sensitive to air). The exposed and evacuated crumbs were no longer capable of affecting the blue dye solution after treatment with a concentrated urea solution, indicating that a small quantity of adsorbed N_2O_4 or HNO_2, remaining after the vacuum treatment, was re-

sponsible for the reddening of the blue dye. It is to be noted that this same quantity of adsorbed N_2O_4 gave only a poor test for nitrous acid with the sensitive coupling agent.

An undyed acetate rayon taffeta, exposed to N_2O_4 for 15 minutes, thoroughly washed with water, scoured, and then dyed (2/10 per cent dyeing) appeared redder and less blue (after washing and air drying) than a scoured acetate rayon taffeta dyed in an identical bath alongside that used for the former.

C. Sensitivity of Some Aminoanthraquinone Dyes In Solvents To Oxides of Nitrogen

1/10 per cent benzene solutions were made of 1:4 diaminoanthraquinone (purified), the blue 1:4:5:8 tetraaminoanthraquinone (purified in same manner as the 1:4 compound—see Action of Oxides of Nitrogen On Pure 1:4 Diaminoanthraquinone), and the commercial blue dye Celliton Fast Blue AF. Sodium Nitrite reagents were prepared having concentrations of 1 part of nitrite per 10,000, 1 part per 100,000, 1 part per 1,000,000, 1 part per 5,000,000, and 1 part per 10,000,000 of H_2O.

2 ml. of dye solution were poured into clean test tubes. 12 ml. of the nitrite reagent of known dilution added, followed by 5 drops of 1:1 HCl, and the tubes shaken for 30 seconds. A blank was run alongside, 12 ml. of distilled water being substituted for the nitrite. The tubes were kept in the room and compared with the blank. Striking changes to red were observable with the blue dye. The results are tabulated at the bottom of the page. All indicated colors are comparisons with blank.

Effect of Light

Two tubes containing 2 ml. of a 1/10 per cent benzene solution of Celliton Fast Blue AF, 12 ml. of nitrite (1 part per 100,000) were kept from the light, 5 drops of 1:1 HCl added, and the tubes shaken 30 seconds. One tube, B, was then placed in a dark closet and tube A in the ordinary light of the room. The next day, A appears violet, B still blue. Three days later, A is red—no blue; B—blue with violet tint. One month later, B still violet. Repeats gave constant checks.

The above tests conducted with 1:4:5:8 tetraaminoanthraquinone and 1 part per 1,000,000 and 1 part per 5,000,000 solutions of nitrite showed on examination 2 days later that the tube kept in the light was more red, less blue than the one in the dark.

Similar results were obtained in chloroform solution of the dyes.

Influence of Cellulose Acetate

Speculation on the role of acetate rayon in the fading process brought to the fore an interesting question. Would the speed of action or sensitivity of the above tests be increased if to dye solutions made up with cellulose acetate solvents, cellulose acetate was added and dissolved?

2 ml. of a 1/10 per cent solution of Celliton Fast Blue AF in $CHCl_3$ were placed in each of two test tubes, A and B. To tube A was added 2 ml. of $CHCl_3$; to tube B, 2 ml. of a saturated solution of acetate rayon in $CHCl_3$ (solubility of acetate in $CHCl_3$ limited—solution made by refluxing acetate rayon with $CHCl_3$). 12 ml. of 1 part per 100,000 nitrite solution were added to each and then 5 drops of 1:1 HCl. The tubes were shaken for 30 seconds and kept in the room. Within ½ hour, the tube containing acetate rayon was discernibly redder than A (B and A equal to start). Next day, the difference was accentuated, B appearing almost pink and A violet.

D. Action of Nitrogen Oxides On Pure 1:4 Diaminoanthraquinone

A comparatively pure compound obtained from both Zinsser & Co. and DuPont was readily purified in excellent yield by recrystallization twice from dioxane. Shining crystals m.p. 267-268° C. (1:4 diaminoanthraquinone m.p. 268° C.) and Kjeldahl N value of 11.6 per cent (theoretical 11.8 per cent N) were obtained.

A commercial 1:4 diaminoanthraquinone dye obtained from DuPont was purified as follows: 50 parts of H_2O were added for each part of dye, stirred vigorously, and the H_2O heated to 50-60° C. until a fine state of dispersion was obtained. 1 per cent Na_2CO_3 was added until distinctly alkaline to brilliant yellow paper and then NaCl (10 per cent solution) until coagulation sufficient for filtration was obtained. The whole was allowed to stand overnight, filtered, and washed well with cold water until a negative test for chloride was obtained. The product (melting 228-235° C.) was recrystallized twice from dioxane, yielding a pure compound, m.p. 266-267° C.

Action of NO On Suspended 1:4 Diaminoanthraquinone

Petroleum Ether, b.p. 90°-100° C, does not dissolve 1:4 diaminoanthraquinone in the cold (a slight violet tint is acquired by the ether). The same substance, pretreated by exposure to an NO stream for 1½ hours (a

Nitrite Solution	†Violet 1:4 Diaminoanthraquinone	*Blue 1:4:5:8 Tetraminoanthraquinone	Blue Celliton Fast Blue AF
1 part per 10,000	immediate reddening, some brownishness in benzene layer	immediate red	immediate red
1 part per 100,000	immediate reddening of benzene layer—yellow aqueous layer	immediate red	red tint after ½ hour—red in 2-3 days
1 part per 1,000,000	more red compared to blank within 1 hour	tinted red immediately—redder with time	red tint within ½ hour—violet in 4 days
1 part per 5,000,000	no change	red tint immediately	no change
1 part per 10,000,000	no change	no change	no change

†Dye not as ideal for test as blue ones because of large amount of red appearing originally in a 1/10 per cent benzene solution.
*Sensitive to acid, assuming a violet color even with blank. However nitrite test will be much redder. With blank, original color can be restored by addition of concentrated NH_3 within ½ hour of acid addition.

slight action occurs yielding a yellow oily substance on evaporation) followed by N_2, and then distilled from P_2O_5 was found to yield a liquid perfectly inert to NO and therefore satisfactory for use as a suspension medium for 1:4 diaminoanthraquinone.

2.5 g. of pure 1:4 diaminoanthraquinone, m.p. 267° C., were suspended in 120 ml. of petroleum ether (NO pretreated) in a special 3 necked reaction flask (attached at Section II of Diagram I and also connected to a vacuum distillation setup). N_2 was passed through the system for ¾ hour and then NO for 1½ hours in the same manner as that used with the dyeings. By suitable adjustment of stopcocks, a vacuum distillation setup, with the reaction flask becoming a distillation flask was obtained. With an oil bath at 60° C. placed beneath the flask, the petroleum ether was distilled over at 10-20 mm., thereby insuring the removal of dissolved or adsorbed NO before opening the reaction flask to the air. The pressure was regulated by a N_2 feed-in.

The residue I (2.5 g.), not visibly changed in appearance, showed indecisive melting over a range beginning at 230° C. Continued extraction of I with petroleum etser, (b.p. 60-80° C.) yielded an orange filtrate, a slow solvent action being indicated. The filtrate evaporated to dryness on a steam bath yielded a very small amount of an orange brown solid (no definite melting point). The residue remaining after the petroleum ether extractions gave m.p. 263°-265° C. alone, and mixing melting points of 265°-266° C. with different proportions of pure 1:4 diaminoanthraquinone, indicating that the bulk of the residue II was unchanged 1:4 diaminoanthraquinone and the action of NO on the dye was slow.

When 1:4 diaminanthraquinone was dissolved in methyl cellosolve (inactive to NO), and NO passed through followed by a vacuum distillation as above, the same orange brown solid was obtained, but in no better yield.

Recent experiments indicate a marked increase in activity when the 1:4 diaminoanthraquinone is dissolved in a methyl cellosolve solution of dried acetate rayon (2.5 g. rayon in 125 ml. of solvent), a deep orange being observable at the end of the NO passage as the gas bubbles broke. Work is continuing on the isolation of the reaction product.

Action of Mixed Oxides On 1:4 Diaminoanthraquinone

Nitrogen oxides (NO, N_2O_3, N_2O_4) generated by the action of 4N H_2SO_4 on a concentrated sodium nitrite solution (70 g. $NaNO_2$ in 150 ml. H_2O) were aspirated through 2 g. of 1:4 diaminoanthraquinone, m.p. 267° C, suspended in 125 ml. of H_2O for 30 minutes, and the resultant suspension filtered. A deep brown precipitate I (1.8 g. after drying) was obtained. A filtrate II was deep orange and deposited a flocculent orange brown precipitate III on standing. I was washed with H_2O and dried in a vacuum desiccator. Heated, I decomposed sharply with evolution of brown NO_2 (detected by odor and starch iodide paper). The decomposition point observable in a tube was 194° C, a puffed black residue remaining. 20 per cent NaOH added to I yielded a deep purple solution with a strong evolution of a colorless, odorless gas, inactive to starch iodide paper, and not supporting combustion, and therefore apparently N_2. III gave the same reaction. I, suspected of being a diazonium salt, was refluxed with CH_3OH for one hour and filtered hot. A brick red substance was obtained from the filtrate and on recrystallization from ethyl alcohol yielded brown red needles; m.p. 241-242° C, alone or mixed with 1 aminoanthraquinone (m.p. 242° C.). I was refluxed in boiling 1:1 H_2SO_4 for three hours. Filtered, a small dark brown residue and an orange filtrate IV were obtained, the latter becoming red on dilution. A sample of IV made alkaline yielded a deep violet solution (hydroxyanthraquinones are characteristically colored violet by alkali). IV was diluted and $NaHCO_3$ added until the evolution of CO_2 ceased. A bright red precipitate was obtained, which on recrystallization from ethyl alcohol gave red crystals, m.p. 213-215° C. (1 amino-4 hydroxyanthraquinone m.p. 215° C.). It was found advantageous to extract with ether after the addition of $NaHCO_3$ and then recrystallize the material remaining after distilling off the ether.

From the reactions noted above, I appears to be a monodiazonium salt, 1 amino 4 diazonium nitrate. To verify, a monodiazonium salt was prepared by adding to a cold water suspension of 1:4 diaminoanthraquinone the calculated quantity of a solution made by adding solid $NaNO_2$ to cold HNO_3. This gave similar reactions, exploding on heating, giving a deep purple solution with N_2 evolution on addition of alkali, and yielding 1 aminoanthraquinone on refluxing with CH_3OH.

Current experiments indicate that when 1:4 diaminoanthraquinone is suspended in an inert medium (light mineral oil) and dry N_2O_4 (from the action of concentrated HNO_3 on Cu and dried* by passage thru Drierite) passed through, a coffee brown solid, exploding on heating, is obtained. This product, not yet identified, gives none of the reactions of the monodiazonium nitrate formed when aqueous suspensions of 1:4 diaminoanthraquinone are used.

SUMMARY AND DISCUSSION

The fading action of pure individual nitrogen oxides on 1:4 diaminoanthraquinone (violet) and Celanthrene Brilliant Blue FFS dyeings has been studied. Nitrous Oxide was found to have no action. Nitric Oxide (spectroscopically pure) was observed to cause a slow reddening, increasing with time, and strikingly similar to actual gas fadings. When the fabrics were dried to remove all moisture, a similar but slower action took place. It appears that the NO action is twofold: (1) a fading action caused by the NO itself as evidenced by the action of the gas on dyed fabrics without moisture, and (2) a

*N_2O_4 will react with many drying agents. The authors found that on conducting N_2O_4 (prior passage thru Cu removed any HNO_3 spray) through $CaCl_2$, HCl was formed and readily detected by passing the gas stream into $AgNO_3$. This would explain the admittedly strange observance of Rowe and Chamberlain[2] that burnt gas fumes (containing oxides of nitrogen), dried by passing through $CaCl_2$ had a much more pronounced fading action on dyeings than moist fumes.

(Continued on Page 664)

THE PLANOFLEX

A Simple Device for Evaluating the Pliability of Fabrics

EDWIN C. DREBY*

The Planoflex, a simple device for measuring the extent to which a fabric can be distorted in its own plane without producing wrinkles on its surface, was developed to evaluate the pliability of woven fabrics. Results of measurements on a series of cotton percales show an 88 per cent correlation with their tactual pliability ratings. Comparison of the Planoflex with the Schiefer Flexometer and the Peirce Hanging-Heart Loop methods for evaluating pliability showed it to be as good as or better than these instruments with respect to the extent of the correlation between measured values and tactual pliability ratings, sensitivity to small differences in pliability, and ease of operation. The Planoflex may be used for testing all woven fabrics except those that are heavily starched.

I. INTRODUCTION

DURING a study of the evaluation of the "hand" or "feel" of fabrics by objective means, particularly with respect to the pliability of fabrics or the ease with which they could be bent in the hands, it was observed that fabrics differed in the extent to which they could be distorted in their own planes without producing wrinkles on their surfaces. Furthermore, it was observed that the extent of this distortion for similarly constructed fabrics indicated their ease of bending. The desirability of having a method for evaluating pliability more practical and sensitive than those at present available led to further investigation of this distortion characteristic and resulted in the development of the Planoflex, which is described in this paper.

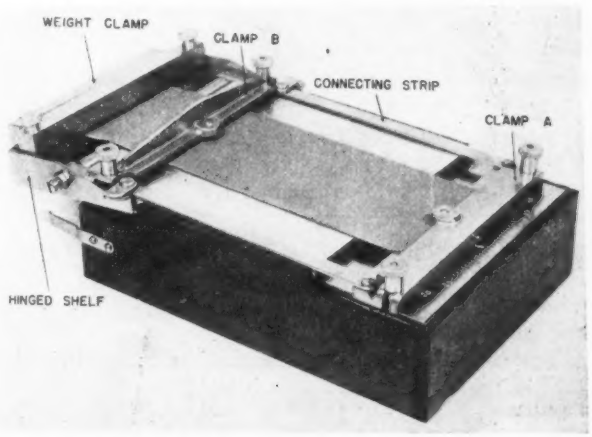
Pliability is one of the components of hand usually judged by handling a fabric and it depends chiefly on the ease of bending or the flexibility of a fabric.† It depends also on a fabric's thickness and weight and, less directly, on its compressibility and surface friction. Since measurements of the ease of bending of fabrics by different testing methods involve these other characteristics to varying extents, the criterion of a suitable testing method, aside from its practicability and sensitivity, is the extent to which its results indicate pliability as appreciated by the hands.

Methods for evaluating pliability have been described by Peirce[3], Schwarz[4, 5], Clark[6, 7], Schiefer[8], Gurley[9] and Saxl[10]. They measure either the deflection of a specimen produced by the weight of the specimen itself or the force required to produce a given deflection. The results are affected to a greater or lesser extent by the weight and thickness of the specimen. Some of the methods are not satisfactory for light-weight, soft-finished fabrics and others are considered too insensitive or too difficult to use for many purposes. The Peirce Hanging-Heart Loop method[3] and the Schiefer Flexometer method[8], representative of these two types of methods, were compared with the Planoflex method in the present work.

II. DESCRIPTION AND USE OF THE PLANOFLEX

The Planoflex is shown in Figure 1. It consists of a metal base plate, supported by a wooden frame, to which is fastened a movable clamp, A; a fixed Clamp, B; and a hinged shelf. Clamp A is constrained by two connecting strips to move in an arc of six inch radius in such a way that it remains parallel to clamp B. A weight clamp, supported by the hinged shelf, is used to put the test

Figure 1—Planoflex



*Research Associate for the American Society for Testing Materials at the National Bureau of Standards on the development of methods for the evaluation of textile finishes.

†The terminology used in this paper is that proposed jointly by the American Society for Testing Materials and the American Association of Textile Chemists and Colorists (see American Dyestuff Reporter 29, 560 [1940]). The term "flexibility" is used to designate the physical property of a fabric that has to do with its ease of bending. Although it is not quantitatively defined it would be measured by some objective means. The term "pliable" and "stiff" and their derivatives describe the ease of bending when determined by the hands and thus involve sensitivity of touch and the ability of the nervous system to discriminate between different physical properties of the fabric.

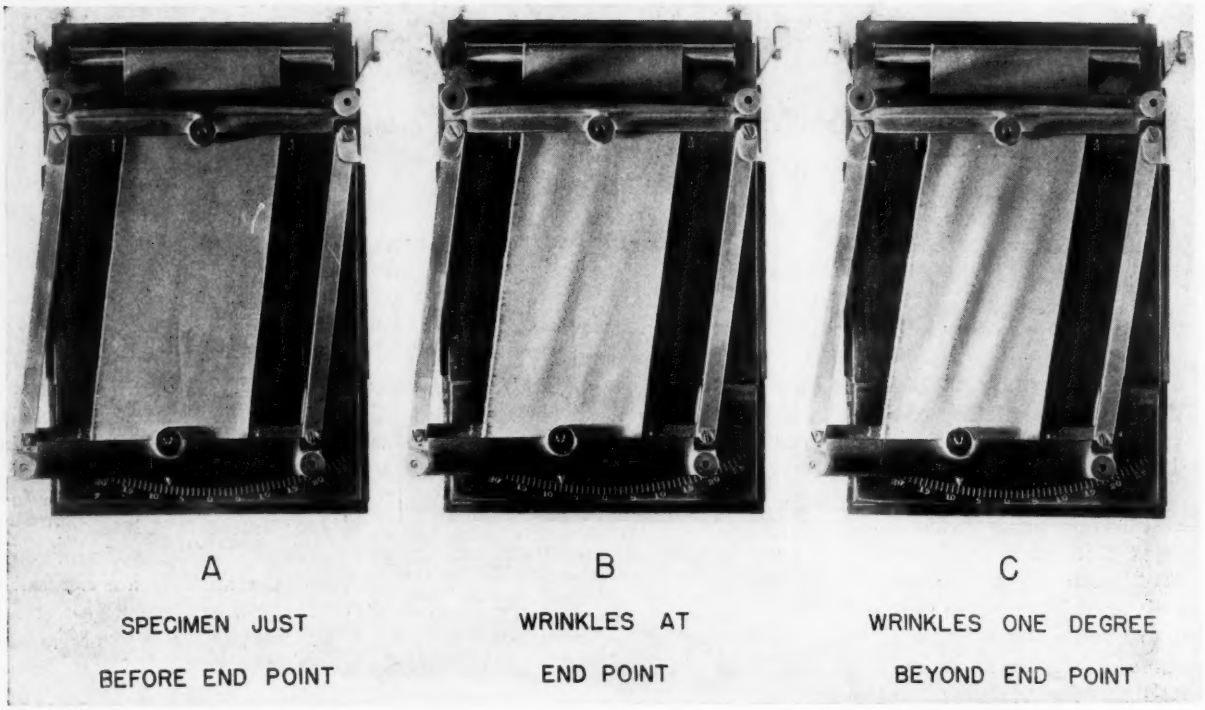


Figure 2—Appearance of specimen in Planoflex at three stages during the measurement: A. Specimen just before end point. B. Wrinkles at end point. C. Wrinkles one degree beyond end point.

specimen under a two-pound tension when it is mounted.

A specimen three inches wide and ten inches long, cut with the long dimension either parallel or perpendicular to the warp yarns of the fabric, is used for the test. A template may be used for cutting the specimen to size. It is essential that at least one edge of the specimen be parallel to the yarns in the lengthwise direction, a condition that is most easily obtained by gently pulling off a few yarns on one or both edges of the test specimen. A variation of ± 1/16 inch in the width of the specimen will not produce any appreciable variation in the result.

A specimen is mounted in the Planoflex as follows: One end is fastened centrally in the weight clamp, care being taken to have the crosswise yarns parallel to the edge of the clamp. Clamp A is moved into the position that makes the lengthwise edge of the specimen intersect corresponding points on the edges of the two clamps, A and B. Scales before the edges of these clamps assist in bringing clamp A into proper alignment. The test specimen is then fastened securely in clamp A. The hinged shelf is released and held in a vertical position by a spring clip so that the weight clamp hangs freely from the end of the specimen, subjecting it to a two-pound tension. Then clamp B is tightened and the specimen is ready for test. The thumb nuts on clamps A and B are on toggle bolts which may be swung out of the way thus permitting easy removal and replacement of the clamp jaws.

To make the measurement, clamp A is moved slowly, first to the left and then to the right, to the angles at which longitudinal wrinkles first appear on the surface of the specimen. These angles, in degrees, are read on the scale below the pointer on clamp A. Greater precision is obtained by repeating this operation two or three times before recording the points at which longitudinal wrinkles first appear. The total angle through which the fabric can be distorted in this manner is the sum of the readings obtained on the left and on the right of the center.

The appearance of wrinkles is more readily observed if a lamp is placed about one foot to either side of the instrument and six inches above its surface. Figure 2 shows how the specimen appears at three stages during the measurement. Figure 2A shows the appearance of a specimen just before the end point on the leftward swing of the movable clamp. Figure 2B shows the appearance of the same specimen when wrinkles were just visible. Two small wrinkles, one in the upper left hand corner and the other in the lower right hand corner of the specimen, appeared shortly after deflection of the specimen. These were ignored. The larger wrinkles running across the entire surface of the specimen determine the end point of the motion. Figure 2C shows the appearance of the same specimen deflected one degree beyond the proper end point. The marked increase in the size of the wrinkles indicates the precision with which the end point can be determined.

The ease and precision with which wrinkles may be determined visually make the Planoflex a very simple instrument to use. However, the end points of motion may be determined objectively, if desired, by using a scanning bar which when raised by a wrinkle completes an

electric circuit. Such a device was found to be satisfactory although it has no particular advantage over the visual method of observing wrinkles.

III. RESULTS OF PLANOFLEX MEASUREMENTS AND EXPERTS' RATINGS OF PLIABILITY

Nineteen 80x80 cotton percales were used for the principle investigation. These fabrics were products of ten different manufacturers, and included printed and piece-dyed fabrics. Their warp counts averaged 86.5 threads per inch, their filling counts averaged 74.5 threads per inch and their weights averaged 4.85 square yards per pound. The variations from these average values were very small and are not believed to have affected the results.

The relative order of these fabrics from the most pliable to the stiffest was determined independently by each of eight textile men experienced in handling fabrics of this type. The average of the eight individual relative ratings for each fabric was taken to represent each fabric's relative pliability. The "average mean deviation"* of the experts' individual ratings for pliability was ±1.6 units of rating. The fabrics are listed in Table 1 in the order of decreasing pliability (increasing stiffness) as determined by the average of the experts' ratings. They were numbered to correspond with their positions in this table.

TABLE 1
Results of Tests with Planoflex, Flexometer and Hanging-Heart Loop on Percales

Fabric Number	*Experts' Average Pliability Rating*	*Dreby Planoflex*	*Schiefer Flexometer*	*Peirce Hanging-Heart Loop*
		Angle	*Torque*	*Bending*
		Degrees	*Gram-Centimeters*	*Length Centimeters*
1	1.9	12.3	101	1.54
2	3.9	12.0	111	1.74
3	4.1	11.3	122	1.80
4	4.5	10.8	120	1.57
5	4.5	10.5	122	1.63
6	5.4	8.5	123	1.49
7	6.6	10.3	117	1.55
8	8.4	16.8	109	1.62
9	8.9	8.5	122	1.76
10	10.4	7.5	143	1.76
11	11.2	6.5	147	1.66
12	11.4	7.0	168	1.82
13	12.4	11.5	122	1.58
14	14.5	4.3	166	1.67
15	15.2	3.0	184	2.07
16	15.5	6.5	194	1.73
17	15.5	3.8	207	1.83
18	17.6	1.8	230	1.82
19	18.3	4.0	214	2.13
Average Mean Deviation	±1.6	±0.4	±7	±0.04

The results of the measurements of the percales with the Planoflex are also given in Table 1. Preliminary studies with these fabrics showed that the measurement of two specimens was adequate to obtain a reproducible, average value of the angle and that it was only necessary to measure specimens cut in one direction since the angles for specimens cut in the fillingwise and warpwise directions different by less than 0.5 degree. Accordingly each reported value is the average of the angles observed for two specimens, both cut with the long dimension in the direction of the warp yarns, since it is easier to cut fabric specimens straight in this direction. The average deviation of the observed angles from their mean varied depending on the magnitude of the observed angle (±0.8 degree when the observed angle was 16.8 degrees to ±0.3 degree when the observed angle was 1.8 degrees). The average mean deviation of the Planoflex results for all fabric specimens was ±0.4 degree. All the measurements were made on samples conditioned at least twenty-four hours in air having a relative humidity of approximately 65 per cent and a temperature of approximately 70 degrees Fahrenheit.

In order to determine the extent to which the results of measurements with the Planoflex correlate with the tactual ratings of pliability, the fabrics were first listed by sample number in the order determined by each of the two methods of ranking, as follows:

Planoflex	8	1	2	13	3	4	5	7	6	9	10	12	11	16	14	19	17	15	18
Experts	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19

According to the Planoflex method, fabric "8" was first with the largest angle (16.8 degrees) and fabric "18" was last with the smallest angle (1.8 degrees). According to the tactual method, fabric "1" was first with the lowest average pliability rating (1.9 units) and fabric "19" was last with the highest average pliability rating (18.3 units). The objective order of the fabrics in each series were then correlated by the procedure described by Kendall†.

The correlation coefficient obtained was 72 per cent. As shown by the arrangement of the fabrics above, fabrics "8" and "13" are the only ones markedly different in the two series. Without these two samples the correlation is 88 per cent, indicating very good agreement between these two methods. These correlation coefficients were computed without regard to the differences between the measured values of the fabrics in each of the two series, many of which were less than the error of measurement. If consideration were given to these small differences in determining the objective order of the fabrics, it would be possible to show an even higher correlation between the Planoflex and tactual methods of evaluating pliability.

The anomalous behavior of fabrics "8" and "13" was also noted in the results of tests with the Flexometer and

*The "average mean deviation" is used in this paper to signify the average, for all fabrics, of the average deviation from the mean of the observations for each fabric.

†The Kendall coefficient of correlation between two series of rankings is given by the equation $\frac{2\Sigma}{n(n-1)}$, where n is the number of members ranked and Σ is computed as follows. The members are put in objective order in the one series which then determines the corresponding order of the rankings for the other series. Each member in turn of the latter sequence of rankings is compared with succeeding members in the sequence. Those pairs in the correct sequence are given a value of +1 and those in the inverted sequence are given a value of —1. The sum of these values is denoted as Σ. The method is described in detail by Schwarz and Winn (Technical Evaluation of Textile Finishing Treatments. III. Use of Rank Correlation for Comparison of Data. American Dyestuff Reporter, 29, P400 [1940]; Textile Research, X, 453 [1940]).

Hanging-Heart Loop methods, which will be given later. The agreement in results among the three test methods on the one hand and among the eight experts on the other as to the relative positions of these two fabrics in the series indicates that some characteristic or condition of these fabrics, not present in the others, has entered into the determination of their pliabilities. The differences between the number of yarns per inch, weight, thickness, coefficient of friction, resilience and compressibility of these fabrics and the respective properties of the other fabrics have been examined but they do not offer any explanation of the lack of agreement between measured and tactual ratings of these fabrics.

To compare the relative sensitivities of the Planoflex and the hands to the differences in pliability of these fabrics, the ratio of the spread of values obtained to their average mean deviation was determined for each series of values. This ratio is an indication of the number of distinct regions within the range of pliability exhibited by these fabrics which might be detected by the method of measurement. The data for the Planoflex gave a ratio of 37 whereas the tactual data gave a ratio of only 10. The sensitivity of the Planoflex relative to the hands may not be as great as indicated here, but it is apparent that it is considerably more sensitive.

IV. COMPARISON OF THE PLANOFLEX AND OTHER METHODS FOR EVALUATING PLIABILITY

To compare the Planoflex with other testing devices for evaluating pliability, the series of nineteen 80x80 cotton percales were measured with the Schiefer Flexometer and the Peirce Hanging-Heart Loop.

The Schiefer Flexometer is an instrument for measuring the torque exerted by a pair of specimens, so mounted as to balance out their weight, when folded to some predetermined angle. Preliminary studies showed that the geometric mean of the torques for an angle of fold in degrees equal to 430 times the thickness of the fabric in inches for warpwise and fillingwise directions gave the most satisfactory results. Four pairs of specimens of each fabric were measured, two prepared with the long dimension in the direction of the warp yarns and two with the long dimension in the direction of the filling yarns. The geometric mean of the average values for warpwise and fillingwise directions are reported in Table 1. The average mean deviation of the Flexometer results for all fabric specimens was ± 7 gram-centimeters.

With the Peirce Hanging-Heart Loop method, the extension of a strip of fabric in the form of a heart-shaped loop is measured, the extension being produced by the weight of the fabric itself. Four specimens of each fabric were measured, two prepared with the long dimension in the direction of the warp yarns and two with the long dimension in the direction of the filling yarns. The geometric mean of the average values for warpwise and fillingwise directions are reported in Table 1. The average mean deviation of the Hanging-Heart Loop results for all fabric specimens was ± 0.04 centimeters.

The correlation between the order of the fabrics determined by these two methods and the order determined by the tactual pliability ratings was determined by the Kendall method described before. For all nineteen fabrics the Flexometer showed a correlation of 79 per cent and the Hanging-Heart Loop, 49 per cent. Fabrics "8" and "13" were displaced in the same direction relative to the other fabrics by the Flexometer results as they were by the Planoflex results, and they also accounted for most of the disagreement between the Flexometer ranking and the experts' ranking of the percales. Of the same two fabrics, only "13" showed marked disagreement between the Hanging-Heart Loop ranking and the experts' ranking of the percales. When both these fabrics were removed from the series, the correlatoin coefficient was 88 per cent for the Flexometer and 51 per cent for the Hanging-Heart Loop. Thus the Planoflex and Flexometer methods are about comparable with respect to the correlation of their results with tactual pliability ratings and somewhat better than the Hanging-Heart Loop method.

To compare the sensitivities of these methods with the Planoflex and the hands, the ratio of the spread of values obtained to their average mean deviation was determined for each series of values as described before. The Flexometer data gave a ratio of 18 and the Hanging-Heart Loop data a ratio of 16 compared with the 37 for the Planoflex and the 10 for the hands. Each of the three testing methods is more sensitive than the hands and the Planoflex is most sensitive.

In addition to the differences between the Planoflex, Flexometer and Hanging-Heart Loop methods with respect to the correlation of their results with pliability and their sensitivity, there are several differences with respect to their ease and convenience of operation that are of considerable importance in applying them to routine testing. The Planoflex, insofar as it has been tested on different types of fabrics, is the only method that gives results which are for all practical purposes independent of the warpwise or fillingwise direction. All of the area of the specimen is distorted during the test as compared to the relatively small part of the fabric specimen bent in the other tests. These conditions permit the measurement of fewer specimens to obtain a reproducible average value. The operation of cutting out and setting up a test specimen is done very easily. The instrument is direct reading. A complete test, including the preparation and measurement of three specimens of a fabric, can be completed in less than five minutes, excluding the time for conditioning of the specimens. The mounting of the specimens for the Flexometer and their insertion in the instrument are delicate and tedious operations. The measurement itself is easily made but there are subsequent corrections for zero points and spring calibrations that have to be made to obtain the value that is used as the measure of pliability. The Hanging-Heart Loop method utilizes the simplest apparatus. A definite technique in handling specimens

(Continued on Page 665)

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NOVEMBER 24, 1941

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CALENDAR OF COMING EVENTS

Meeting, Philadelphia Section, Hotel Philadelphia, December 5, 1941.

Meeting, Northern New England Section, December 12, 1941

Meeting, New York Section, Swiss Chalet, Rochelle Park, N. J., December 5, 1941. P. J. Wood will read the prize-winning paper entered by the New York Section in the Intersectional Contest.

Meeting, Southeastern Section, Atlanta, Ga., December 6, 1941.

Photos by Robert A. Lemieux and M. D. Reeser.

Twenty-first

ANNUAL MEETING

AND CONVENTION

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Auspices of Piedmont Section

PINEHURST, N. C.

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Nature of the
RESISTANCE OF WOOL
to Digestion by Enzymes

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ABSTRACT

Wool and other hair fibers belong to the class of proteins called keratins, and characteristically are extremely resistant to digestion by enzymes. However, certain living organisms, such as the common clothes moth, the carpet beetle, and several molds, readily attack wool. Such destruction apparently is accomplished by means of enzymes produced by these organisms. Investigation has now shown that wool fibers that have neither been injured mechanically nor modified chemically, are resistant to attack by enzymes and that this resistance is dependent upon at least two factors. One factor is the resistance of the outer layer or cuticle of the individual fibers. The other factor is the peculiar chemical structure of wool, in which main chains of molecules (polypeptides) are linked together by disuldfide cross-links formed by pairs of sulfur atoms, to form a three-dimensional network.

When the outer layer of a wool fiber is damaged by mechanical means, the fiber becomes susceptible to attack by enzymes. Under these conditions only a certain small portion of the wool is digested, but nevertheless the fibers are considerably weakened and their fibrous structure is partly destroyed. Even more deleterious are chemical changes that break the disulfide crosslinks. After such changes the wool can be rapidly and almost completely digested.

The results suggest that chemical operations that tend to break disulfide cross-links, such as scouring with alkalies, or bleaching with peroxide should tend to decrease the resistance of wool to attack by biological agents. These results are also in agreement with the conclusions of other investigators, who have shown that moths digest wool through a process which involves rupture of the disulfide groups in the intestine of the moths previous to enzymatic digestion.

Certain chemically-modified wools, in which the disulfide cross-links, which are relatively unstable chemically, have been replaced by new crosslinks of greater chemical stability, were found to have an enhanced resistance to attack by enzymes and other biological agents.

I. INTRODUCTION

PROTEINS of the class called keratins, of which wool is a member, are so characteristically resistant to digestion by enzymes, that this phenomenon is usually included in the definition of the keratin group[1]. The exact reason for this resistance has not been entirely clear, but on the basis of earlier work on wool it seems due to a stability resulting for the presence of disulfide cross-linkages between the polypeptide chains of the protein[2, 3], or to a resistance to diffusion of the enzyme into the fibers, brought about by an impermeable outer layer of scales, or by the walls of the cells composing the fiber. For example, wool previously treated with alkali has been reported by Meunier, Chambard, and Comte[4], and by Fromageot and Porcherel[5] to be disintegrated into spindle-shaped cells by the action of preparations of pancreatic proteinases. Products resulting from the oxidation of human hair by solutions of bromine in glacial acetic acid, or by solutions of hydrogen peroxide in 0.4 *N* sulfuric acid, have been described by Stary and by Waldschmidt-Leitz and Schuckmann[6] as digestible by trypsin. An enzyme discovered by Linderstrom-Lang and Duspiva[7] in the intestinal tract of the clothes moth was found capable of digesting wool in an alkaline and strongly reducing environment. Goddard and Michaelis[8] found that the amorphous reduction products obtained from wool by the action of alkaline thioglycolate solutions, or of other alkaline reducing agents, were digested by pepsin or trypsin. More recently, Routh and Lewis[9, 10] observed that wool powdered by prolonged grinding in a ball mill was changed chemically as well as physically, with the result that it became partly digestible.

Although all of the above-mentioned treatments affect the disulfide groups none of them can be considered to involve these groups alone, so it cannot be finally concluded on the basis of the earlier work that the disulfide cross-linkages are responsible for the resistance of wool protein to digestion by enzymes. Nor can the influence of histological structure be evaluated since those treatments which destroy the fiber structure, such as grinding in a ball mill or reduction in strongly alkaline thioglycolate solution, produce other far-reaching changes as well.

There are still other barriers to drawing exact conclusions from the earlier studies. The preparations of enzymes used have usually not been pure crystalline substances, but have consisted of crude concentrates[4, 5, 8, 11]. Moreover,

the methods available for detecting attack by enzymes have not been very sensitive, since they have depended on measurement of loss in weight[4], of determination of material not precipitable by sulfosalicylic acid[8], or merely of microscopic observation of the extent of disintegration[11]. Such methods are satisfactory when a considerable portion of the protein is digested, but are inadequate when the extent of digestion is small.

In the present investigation it was possible to overcome most of these objections. Chemical reactions that rupture disulfide bonds and minimize the possibility of secondary chemical reactions have recently been developed in this laboratory[3]. The development of methods for preparing crystalline enzymes by Northrop[11] and by Balls and Lineweaver[12] has made possible the use of preparations of enzymes of known identity and purity. Finally, it was possible to follow the attack of enzymes on the wool protein by noting changes in the mechanical properties of the fiber.

II. EXPERIMENTAL PROCEDURE

1. Materials

The wool fibers used in the present study were a portion of the lot used in previous investigations in this laboratory[3, 13]. This wool had been subjected to no chemical or mechanical treatment other than successive extraction with alcohol and with ether, followed by washing with water at 40° C.

Crystalline pepsin, trypsin, chymotrypsin and papain* were used in this work. The papain preparation consisted of a suspension of the crystalline enzyme in a 0.02 *M* solution of sodium cyanide.

The solutions of pepsin with which the fibers were treated contained 1 mg. of crystalline enzyme per ml. of a solution of 0.1 *M* potassium chloride, and were adjusted to a pH value of 1.5 by the addition of hydrochloric acid. The solutions of crystalline trypsin and chymotrypsin each contained 1 mg. of the crystalline enzyme per ml. of a 0.1 *M* solution of potassium phosphate at a pH value of 7.0. The solutions of crystalline papain were prepared from the suspension described above, by diluting it with water to a concentration of 0.16 mg. of protein nitrogen per ml., and adjusting to pH 7.0 by the addition of dilute acetic acid. The addition of small amounts of merthiolate effectively prevented the growth of bacteria in all of these solutions.

A commercial trypsin† was also used in some experiments. In these experiments, 10 mg. of enzyme preparation per ml. of 0.05 *M* potassium phosphate at pH 7.0 was used. The solutions of commercial trypsin were kept sterile by the addition of small amounts of thymol.

*We are indebted to Dr. J. H. Northrop of the Rockefeller Institute for Medical Research for a gift of crystalline trypsin and chymotrypsin, and to Dr. A. K. Balls of the U. S. Department of Agriculture for a gift of crystalline chymotrypsin and papain.

†The term "commercial trypsin" is used in this paper to indicate a relatively crude preparation of enzyme material prepared from pancreatic juice and available from commercial sources.

2. Methods

a. Detection of Attack by Enzymes

The attack by the enzymes was followed by measuring the stress-strain characteristics of the fibers at different stages of treatment. This method has the advantage that it can detect amounts of digestion too small to be detectable by the usual methods. It** depends upon the fact that a wool fiber that has been immersed in water or a neutral buffer solution and stretched under load until it is elongated 30-per cent will return almost to its original length when the load is removed. If the fiber is allowed to relax in the unstretched state in water or in the neutral buffer solution for about 24 hours and then again stretched until elongated 30-per cent it is found that the same amount of energy (within about 1 per cent) is required for the second stretching as for the first. However, if some treatment that weakens the fiber is interposed between the two stretchings, it is found that a lesser amount of energy is required the second time. In such a case, the ratio of the energy required for the second stretching to that required for the first is known as the *30-per cent index* of the fiber. A fiber that has been stretched the first time is hereafter referred to as a *calibrated fiber*.

All stress-strain measurements were made on fibers in 0.2 *M* phosphate buffer solution at pH 7.0. Calibrated fibers that had been treated with solutions of enzymes were always washed thoroughly with distilled water, and then kept in the phosphate buffer solution at pH 7.0 for at least 20 hours before stretching them a second time.

b. Chemical Treatments

Methods for the preparation of derivatives of wool in which the disulfide cross-linkages have been ruptured without visibly affecting the fiber structure have previously been described in detail[3]. The methods involve reducing the wool with thioglycolic acid solutions followed by treating the reduced product with an alkyl halide. The reactions appear to involve only the disulfide groups of the cystine in wool, and may be represented by the following equations:

(1) $W—S—S—W + 2HS—CH_2—COOH \longrightarrow 2W—SH + (HOOC—CH_2—S)_2$

(2) $W—SH + RX \longrightarrow W—SR + HX$

(3) $W—SH + CH_2X_2 \longrightarrow W—S—CH_2—S—W + 2HX$

where W represents the portions of the wool molecule connected by the disulfide groups, R an alkyl group, and X a halogen atom.

The reduced, and the reduced and alkylated wool fibers used in the present investigation contained between 4 and 6 per cent of unchanged cystine. The cystine content of the untreated wool was 12.4 per cent. The reduced and reoxidized wool fibers were prepared by reducing wool to about this same cystine content, and reoxidizing with oxygen as previously described[3].

c. Mechanical Treatments

The mechanically "injured" fibers were prepared by placing calibrated fibers on a glass plate, and tapping them

**The mechanical details are presented elsewhere[18].

at about 6 places along their length with a rounded glass rod. Such fibers, on examination under the microscope, appeared to be injured since crevices were formed and cuticle scales lost in the tapped regions. At this point in the procedure, the mechanically injured fibers were again calibrated, and those that had 30-per cent indices less than 0.96 were discarded.

d. Enzyme Treatments

Each fiber, after the calibration and the subjection to either mechanical or to chemical treatments was placed in a small test tube. One ml. of the solution of enzyme was added and permitted to act for the specified period at 20-25° C. In order to be sure that the effects observed were the results of the action of enzymes, control experiments were always carried out, in which another group of calibrated fibers was exposed to the action of identical solutions, except that no enzyme was present.

III. RESULTS AND DISCUSSION

The results of the action of the different enzymes upon wool fibers are summarized in the following sections.

1. Crystalline Pepsin

During periods up to 10 days, solutions of crystalline pepsin had no appreciable effect upon the untreated fibers, as indicated by the fact that the 30-per cent indices remained high averaging 0.96 (Table 1). When the treatment was prolonged to 30 days, the fibers disintegrated at the slightest touch. However, fibers in a similar but enzyme-free solution adjusted to a pH value of 1.5 were found to be considerably weakened, the 30-per cent index falling to 0.77, and such fibers, when transferred to pepsin solution, were almost immediately attacked by the enzymes. It is thus seen that undamaged fibers are not attacked by pepsin, but that solutions acid enough for the optimum activity of pepsin gradually attack the fibers and make them susceptible to the action of the enzyme.

TABLE 1
Effect of Solutions of Crystalline Pepsin Upon Wool Fibers Subjected to Various Treatments

Previous Treatment	*Duration of Enzyme Treatment*	*30-Per Cent Indices*	
		Enzyme-treated	*Controls*
	Days		
None	10	0.96	0.95
None	30	*	0.77
Mechanical injury	10	*	0.96
Reduction	4	*	0.62
Reduction and reoxidation	10	0.94	0.94
Reduction and CH_3I	2	*	0.48
Reduction and CH_2I_2	14	0.93	0.93

*Fibers broke before or during second calibration. See text.

Crystalline pepsin readily attacked mechanically damaged fibers, and weakened them so that they broke at 5- to 10-per cent elongation. The broken ends of the mechanically damaged, pepsin-treated fibers showed ragged breaks, at which clearly outlined cortical cells were visible, and not the sharp, straight break characteristic of untreated fibers, as may be seen by comparison of Fig. 1-a with Fig. 1-b.

The effect of reduction, or of reduction followed by methylation, was to render fibers extremely susceptible to digestion by crystalline pepsin. Fibers that had been subjected to either of these chemical treatments and then to the action of pepsin seemed, while still immersed in the enzyme solution, not to have changed greatly in appearance, but were so fragile that attempts to remove them caused them to break into small pieces. A comparison of Fig. 2-a with Fig. 2-b shows the marked changes produced by the enzyme, including digestion of cortical material, liberation of some cortical cells, and formation of empty tubes of scales. The photographs of cross-sections, Fig. 3-a, 3-b, and 3-c demonstrate progressive digestion by pepsin of the cortex of reduced and methylated wool fibers.

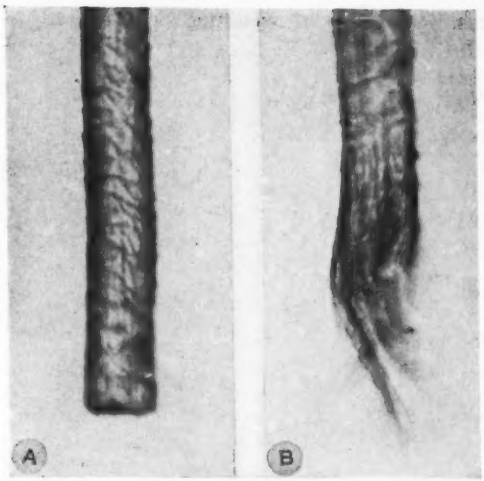

Fig. 1—Broken ends of untreated wool fibers (A) and mechanically damaged wool fibers (B) after treatment with pepsin. Magnification X 250.

Fibers that had been reduced and reoxidized were as stable as untreated fibers toward solutions of crystalline pepsin. Fibers into which new cross-linkages introduced by reduction followed by treatment with methylene iodide (according to eq. 3) were likewise not attacked.

2. Crystalline Chymotrypsin

Pepsin is most active in acid solution, but acid solutions slowly attack the wool and increase its susceptibility to the action of the enzyme. To avoid this complication, it appeared desirable to study the effect upon wool of an enzyme active at a neutral pH value. Crystalline chymotrypsin, which occurs in pancreatic juice along with crystalline trypsin and other enzymes, is active at pH 7.0. Although this enzyme was found to attack reduced and reduced and methylated wool somewhat less rapidly than does pepsin, its action resembled that of pepsin in that it digested the cortex but not the cuticle. Furthermore, untreated wool fibers and those that had been reduced and alkylated with methylene iodide were not attacked (Table 2).

3. Crystalline Papain

Neither untreated wool, nor any derivative of wool studied, was attacked by solutions of crystalline papain. In all cases, the 30-per cent indices of the enzyme-treated fibers were very close to those of the "control" fibers. The derivatives included wool that had been reduced,

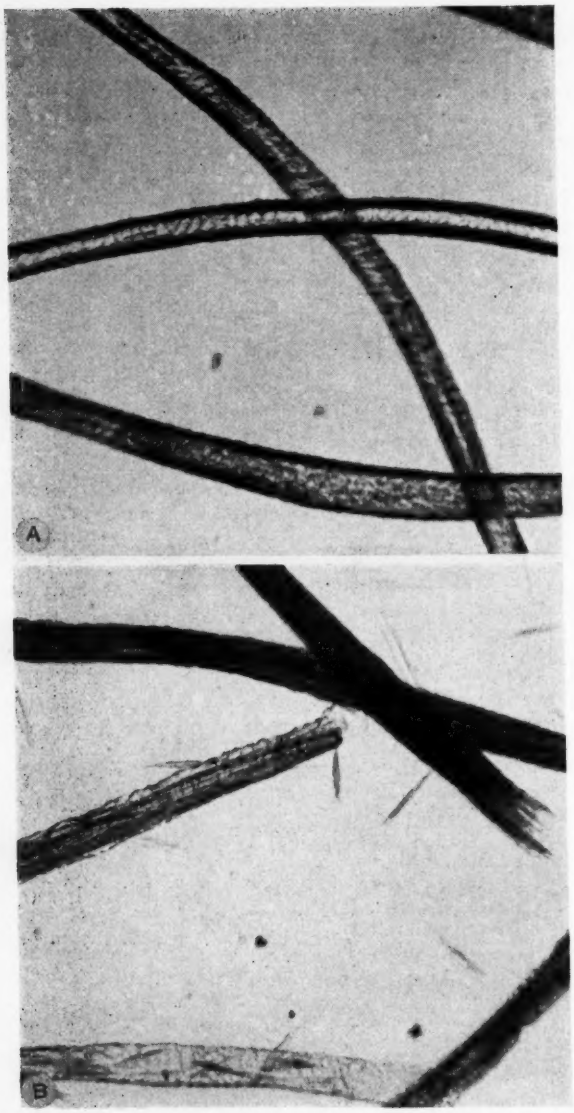

Fig. 2—Untreated wool fibers (A) and reduced and methylated wool fibers (B) after treatment with pepsin. Magnification X 150.

TABLE 2
Effect of Solutions of Crystalline Chymotrypsin Upon Wool Fibers Subjected to Various Treatments

Previous Treatment	Duration of Enzyme Treatment	30-Per Cent Indices	
		Enzyme-treated	Controls
	Days		
None	7	0.99	0.99
Mechanical injury	7	*	0.95
Reduction	4	*	0.55
Reduction and reoxidation.	7	0.97	0.99
Reduction and CH_3I	4	*	0.41
Reduction and CH_2I_2	7	0.89	0.91

*Fibers broke before or during second calibration.

reduced and reoxidized, reduced and methylated, and reduced and treated with methylene iodide (Table 3).

4. Crystalline Trypsin

Untreated wool fibers were not attacked by trypsin, even after prolonged exposure of the fibers to sterile solutions of this enzyme. Similarly all of the treated

Fig. 3—Cross-sections of wool fibers treated with pepsin.
A. Sections of untreated fibers treated with pepsin for 30 days.
B. Sections of reduced and methylated fibers treated with pepsin for 10 days.
C. Sections of reduced and methylated fibers treated with pepsin for 30 days. Magnification X 450.

TABLE 3
Effect of Solutions of Crystalline Papain Upon Wool Fibers Subjected to Various Treatments

Previous Treatment	Duration of Enzyme Treatment	30-Per Cent Indices	
		Enzyme-treated	Controls
	Days		
None	7	0.99	0.99
Reduction	7	0.55	0.55
Reduction and reoxidation.	7	0.94	0.94
Reduction and CH_3I	7	0.43	0.43
Reduction and CH_2I_2	7	0.83	0.89

fibers, except those that had been reduced alone, were unaffected. Reduced fibers, however, appeared to be slightly attacked since many of them broke at 20- to 25-per cent elongation (Table 4).

Although the optimum pH value for the action of trypsin is nearer 8 than 7, the trypsin solutions were adjusted to the latter pH value in most of the experiments in order to avoid extraneous effects due to alkali. Further experiments have now shown that solutions of crystalline trypsin do not digest untreated or reduced and methylated wool even at pH 8.0.

TABLE 4
Effect of Solutions of Crystalline Trypsin Upon Wool Fibers Subjected to Various Treatments

Previous Treatment	Duration of Enzyme Treatment	30-Per Cent Indices: Enzyme-treated	30-Per Cent Indices: Controls
	Days		
None	14	0.98	0.98
Mechanical injury	10	0.95	0.96
Reduction	7	*	0.60
Reduction and methylation	7	0.48	0.55

*Fibers broke after 20- to 25-per cent extension.

5. Commercial Trypsin

Commercial trypsin is a relatively crude preparation made from pancreatic juice and consists of a mixture containing proteolytic enzymes active at a pH value of 7.0. Since it has been used extensively by earlier investigators, it appeared advisable to conduct a few experiments with it in the present investigation. The effects of commercial trypsin upon the fibers are much like those of crystalline chymotrypsin. Fibers that were untreated, reduced and reoxidized, or reduced and treated with methylene iodide were not affected by the enzyme (Table 5). Reduced and methylated fibers were readily attacked. Commercial trypsin acted more slowly, however, and never produced as complete digestion of the cortex of the fibers as did crystalline pepsin. Since commercial trypsin attacks wool and crystalline trypsin does not do so, it is evident that some constituent other than crystalline trypsin, possibly crystalline chymotrypsin, is responsible for the action of the commercial product upon the fiber.

TABLE 5
Effect of Solutions of Commercial Trypsin Upon Wool Fibers Subjected to Various Treatments

Previous Treatment	Duration of Enzyme Treatment	30-Per Cent Indices: Enzyme-treated	30-Per Cent Indices: Controls
	Days		
None	7	0.99	0.99
Mechanical injury	7	*	0.96
Reduction and reoxidation	7	0.89	0.89
Reduction and CH_2I	2	*	0.47
Reduction and CH_2I_2	7	0.91	0.91

*Fibers broke before or during second calibration.

IV. DISCUSSION

The experiments described in the preceding sections show that wool fibers, when chemically unchanged and mechanically intact, are not attacked by sterile solutions of any of the enzymes studied. The present methods permit more exact interpretations and reveal some of the reasons why earlier experiments have sometimes indicated that wool is digestible by enzymes. Since detailed information has generally not been given in earlier published accounts, no attempt is made to consider each report individually. Results based upon wool that has previously been treated with alkali[4, 5, 15, 16] or with other chemical agents which do not react solely with disulfide groups[4, 6, 9, 10], or upon wool that has received mechanical treatment[11], do not provide clear evidence regarding its stability to enzymes. Particularly noticeable in the literature is the absence of statements regarding the sterility of the enzyme solutions. That this is important is shown by the fact that wool kept in a solution of commercial trypsin to which a small crystal of thymol has been added is not noticeably attacked after several weeks and that wool in a similar, but thymol-free solution shows rapid digestion and evolution of hydrogen sulfide. The effect is apparently a result of the action of microorganisms which attack disulfide groups as well as hydrolyze peptide linkages.

Modified wool fibers may be attacked by enzymes in at least two different ways, depending upon whether the fibers have been modified by mechanical or by chemical means. Mechanically injured wool was attacked by pepsin, but was only broken down into spindle-shaped cortical cells. Even after several months, over 90 per cent of the wool could be recovered in the form of these cells. However, chemical modification that involves rupture of the disulfide cross-linkages of the wool renders the cortex of the fibers completely digestible. For example, reduced and methylated wool (cystine content 2 per cent) was almost completely digested by pepsin after two weeks. The residue, which consisted principally of scale substance, amounted to only 4 per cent of the weight of the wool. Since the effects of the two modes of attack are very different, they are discussed separately in the following sections.

1. Digestion of Mechanically Injured Wool Fibers

Pepsin and chymotrypsin attack mechanically injured fibers, but in a way best discussed after considering the histology of the fibers. Wool fibers are not homogeneous but consist of cellular units, arranged in three layers; an outer cuticle consisting of scale cells; a middle region called the cortex, made up of spindle-shaped cortical cells; and a central core or medulla. In many types of wool, the medulla may be very small or absent. After mechanical injury, the fibers are attacked and free cortical and scale cells are liberated, but these do not appear to be digested by the enzymes. An attack of this type apparently does not result in the digestion of the principal fibrous protein of the wool; rather the appearance of the product suggests that an intercellular substance may have been digested. Such an explanation has already been offered for the action of commercial trypsin on wool by Stakheeva-Kaverzneva and Gavrilov[15], and by Speakman and McMahon[16].

Apparently the impermeability of the cuticle is an important factor in the resistance of chemically unchanged fibers to digestion by enzymes. Mechanical injury of the cuticle or, as will be discussed later, rupture of the disulfide cross-linkages, increases its permeability and facilitates attack. Further evidence of this impermeability is shown by the fact that the cut ends of fibers (either chemically unchanged, or reduced and methylated) are more readily attacked than other parts[17].* The permeability of the cuticle undoubtedly varies considerably with

*The penetration of large dye molecules into wool fibers seems to be analogous, since, as has been shown by Millson, Royer and Wissemann[18], the rate of penetration is increased in injured fibers. Likewise, the rate of penetration of dye into wool in which disulfide cross-linkages have been ruptured is also increased.

different types of wool, since these are attacked by enzymes and also absorb dye at very different rates under identical conditions. Damage to the cuticle during chemical or mechanical processing of commercial wools probably contributes to the conflicting results reported in the literature concerning the attack of wool by enzymes.

2. Digestion of Chemically Modified Wool Fibers

The digestion of cortical material was almost completely observed after the disulfide cross-linkages had been broken by reduction, or by reduction followed by methylation. When the cross-linkages were rebuilt, either by reoxidation of the sulfhydryl groups to disulfide groups, or by their conversion to *bis*-thioether groups (—S—CH_2—S—), the resistance to digestion of the original wool was restored.* Thus, the resistance appears to be due, not to the chemical nature of the groups involved. but to the existence within wool of a compact three-dimensional polymeric structure, which is a result of the presence of disulfide cross linkages between polypeptide chains.

A more detailed consideration of the chemistry of polymerization supports this hypothesis. Reduced wool probably consists of polypeptide chains containing cysteine residues. In the sense of Carothers'[19] definition, these polypeptides are linear polymers bearing functional groups capable of reacting with each other to yield a three-dimensional polymer. That is, oxidation of the reduced wool would form disulfide cross-linkages between different polypeptide chains and yield polymers of high molecular weight.

The formation of polymers of high molecular weight from molecules that bear more than one functional group is favored when the concentration of a reactant is high. At lower concentrations, lower degrees of polymerization and even reactions to form monomers are to be expected[20]. This means that the formation of disulfide cross-linkages between different polypeptide chains should be favored in reduced fibers because the concentration of the reactant (reduced protein) is extremely high. The reoxidation of wool by the methods of Goddard and Michaelis, in which reduced wool is dissolved in alkali and then treated with an oxidizing agent, should result in a lower degree of polymerization, and should favor the formation of disulfide links between different parts of single folded chains. That the amorphous products obtained by these authors may be of this nature is suggested by their high solubility in dilute solutions of acids or alkalies, in which reoxidized wool fibers of the type obtained in the present study are almost completely insoluble.

The resistance of the cortex of wool to digestion by enzymes then appears to be due to its compact three-dimmensional polymeric structure. A structure of this sort might resist attack by enzymes through two mechanisms: (1) by keeping the molecules of enzyme from penetrating the structure (2) by interfering with free rotation of the units of the peptide chains into the special configurations believed to be favorable for enzyme action[21].

Goddard and Michaelis have suggested that a definite physical pattern imparts to wool protein its resistance toward enzymes. The present work indicates that all that may be required is the formation of polymers of extremely high molecular weight and compact structure.

*Wools of this type have now been shown to be even more resistant to enzymes, bacteria, fungi and moths than the original wool[22].

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Gas Fading—

(Continued from Page 650)

fading action caused by the slow hydrolysis of NO with the water content of the fabric (normal regain about 6.5 per cent), giving rise to fading active HNO_2 as follows:

$$4NO + 2H_2O \longrightarrow 2HNO_2 + H_2N_2O_2$$

The latter decomposes:

$$H_2N_2O_2 \longrightarrow N_2O + H_2O$$
$$3H_2N_2O_2 \longrightarrow 2N_2O_3 + 2NH_2$$
$$NH_3 + HNO_2 \longrightarrow N_2 + 2H_2O$$

Evidence for the second type of action is the continued fading of the violet dyes, approaching an orange red after several months (HNO_2 itself causes a fading to yellow via orange). This is further supported by the fact that exposure tubes containing 1:4 diaminoanthraquinone dyed fabrics (moisture present) in NO almost immediately fade to a yellow when placed in an oven at 100° C., whereas the same fabrics (no moisture present), similarly exposed, do not change their previously acquired reddish violet

color. Moser has shown that the hydrolysis of NO is greatly increased by heat[14].

Light has been shown to accelerate the fading action of NO. Solvent solutions of dyes exposed to "oxides of nitrogen" also indicated an accelerated fading action in the light. This indicates the possible importance of light in gas fading. Further work along these lines is necessary.

N_2O_4 was found to have an instantaneous and drastic fading action on aminoanthraquinone dyeings. When undyed cellulose acetate was exposed to N_2O_4, the formation of free acetic acid and cellulose nitrate was detected, though only after a severe long exposure. Undyed cellulose acetate, so exposed, had no effect on benzene solutions of the blue aminoanthraquinones, but on dyeing with 1:4 diaminoanthraquinone appeared redder than a control dyeing.

A test procedure for determining the sensitivity of acetate rayon dyes was devised, and a blue dye, 1:4:5:8 tetraaminoanthraquinone was found to be capable of detecting 1 part in 5,000,000 of nitrite. Such a sensitivity test, combined with the now used tests for extent of fading, should be more helpful than the latter alone. These dyes may prove useful for a sensitive qualitative test for nitrite, free acids having been previously neutralized, and reducing agents being absent.

The action of NO on suspended or dissolved (methyl cellosolve) 1:4 diaminoanthraquinone was slight, but preliminary work indicates a markedly increased reaction when cellulose acetate is dissolved in the dye solution. This technique of using dye-cellulose acetate solutions shows promise as a means for investigating gas fading reactions. The advantages are: (1) similarity to actual conditions on a fabric, cellulose acetate being present; (2) increased concentrations of dye, not possible with reaction studies on the fiber.

The action of higher oxides of nitrogen (N_2O_4, N_2O_3) on 1:4 diaminoanthraquinone results in the formation of a 1 amino 4 diazonium nitrate when the dye is suspended in water. The mechanism appears to be the formation of nitrous and nitric acid as follows:

$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$, and then diazotization taking place as though a nitrite and acid were added. The same dye suspended in an inert medium, light mineral oil, yields a product, not yet identified, but not the same as that from water suspensions. Although water is always present in an acetate rayon fabric, study of the reaction mechanism by suspension of the dye in water, presupposes its part in the reaction. Both NO and N_2O_4 cause fadings with dry fabrics. There is need for some caution in accepting diazotization and nitrosation as the reaction until proof of their formation on the fiber. Further work using inert mediums and cellulose acetate solutions should be helpful.

The fact that NO can cause slow fadings indicate its usefulness for studies of fading directly on the fiber. N_2O_4 gives too drastic a reaction, probably several simultaneous reactions. The controllable NO fading can be stopped at any color phase, and a solvent added to extract the faded product, if a suitable apparatus is set up. NO is present in burnt gas fumes since it is the first product of N_2 combustion. It is very important therefore that the air intake and height from burner to chimney in test apparatus be specified so that the NO—N_2O_4 ratio in the gases may be kept fairly constant.

The role of cellulose acetate remains obscure. The action of nitrogen oxides on the acetate appears to be a secondary reaction, yet the dyeing properties of a mildly exposed acetate rayon are changed. In solution (colloidal), acetate rayon still exerts a sensitizing action on dyes exposed to nitrogen oxides. The fact that acetate rayon is a diacetate should not be overlooked, and the influence of other cellulose and lower alcohol esters is worthy of investigation. Salt formation of the ester with the NH_2 group of the dye may be the sensitizing influence.

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The Planoflex—

(Continued from Page 654)

for this test has to be developed to avoid erratic results. The observed values must be converted by means of the formula derived by Peirce to the quantities that indicate pliability.

V. DISCUSSION OF THE BEHAVIOR OF FABRICS IN THE PLANOFLEX TEST

A consideration of the conditions involved in the Planoflex test will make more apparent the uses and limitations of the Planoflex for evaluating pliability.

The contribution of the physical properties of a specimen to its angle of distortion seem to be of two kinds.

First there is a certain amount of free space between the yarns of the specimen that permits relative rotation of the warp yarns and the filling yarns at their intersections throughout the specimen. The free space available depends mainly on the size of the yarns and the number of yarns per inch. Since the contribution of this freedom of motion to the total angle of distortion is relatively large and practically independent of all but dimensional characteristics of the yarns, it cannot be expected that results with the Planoflex on differently constructed fabrics will be comparable.

After the free space is taken up, however, the yarns themselves are subjected to compression as continued distortion of the specimen reduces its area. Depending

on the physical characteristics of the yarns, a condition of instability is reached that results in a sudden disruption of the surface of the specimen. The ability of the yarns to give during this stage of the distortion is apparently intimately related to their flexural characteristics since on similarly constructed fabrics the results of measurements with the Planoflex, Flexometer and Hanging-Heart Loop are in substantial agreement. Other physical properties of the yarns, notably their surface friction and density, undoubtedly affect the extent of the distortion of the specimen. It would appear that either their effects are too small in proportion to the effects of the flexural properties or their effects complement the effect of the flexural properties in giving values that indicate pliability.

Since it is necessary to put the specimen under tension in order to obtain reproducible results, the specimen of any fabric that is too readily stretched will, after mounting, have a different construction insofar as the test is concerned than the fabric which it is supposed to represent. Thus measurements on fabrics which may have identical construction but which have different extensibilities will not be on a comparable basis.

VI. USES AND LIMITATIONS OF THE PLANOFLEX TEST

The Planoflex is well adapted to testing a wide variety of fabrics as shown by measurements on the following representative types: cotton print cloths, broadcloths, poplins, organdies, twills and sateens; rayon French crepes, twills, satins and spun rayon fabrics of challis-like and linen-like finish; and wool and mixed wool-rayon uniform suitings and shirtings. With the exception of a very few fabrics in some of the groups, the results of measurements with the Planoflex were in agreement with the pliability ratings of these fabrics determined tactually by experts. The order of magnitude of the values obtained for the particular fabrics representing these several types is indicated in Table 2.

TABLE 2

Range of Planoflex Values for Different Types of Fabrics

Fabric	*Range: Degrees*
Cotton:	
80x80 print cloths	2-16
68x72 print cloths	10-25
100x60 broadcloths	8-15
100x40 poplins	12-23
76x72 organdies	36-54
68x76 twills	5-10
65x110 sateens	2-30
Rayons:	
165x72 crepes	29-35
116x67 twills	36-42
225x65 satins	37-44
68x62 spun rayons:	
challis-like	36-43
linen-like	31-35
Wool and Mixed Rayon-Wool:	
Uniform suitings	11-17
Uniform shirtings	20-28

Like other instruments for evaluating pliability, the Planoflex cannot be used indiscriminately to evaluate the relative pliability of fabrics of different construction. By different construction is meant different fiber construction, different yarns per inch in either direction, and different weight. Variations of plus or minus five per cent in either the count or the weight of a group of fabrics should be considered the limits within which the results with the Planoflex are on a comparable basis. With fabrics having greater variations in these properties than the above, the results with the Planoflex should be examined carefully before any significance is attached to them. A few special fabrics, like tracing cloth, in which a heavy coating of starch has cemented warp and filling threads together, will not give measurable results on the Planoflex. Knit-fabrics are too easily distorted and stretched to give values of any significance.

In addition to the use of the Planoflex for quantitatively evaluating pliability, there are two other uses to which the instrument can be applied with distinct advantage: namely, the evaluation of the effect of different finishing agents and technical control during finishing operations.

With a sensitive, reliable instrument for indicating quantitatively the effect of different finishing agents on a fabric, a finisher can select with greater certainty the better finishing agents for his purposes, not only with respect to the desirability of their effects but also with respect to the economy of their use. It should be pointed out that finishing agents have greater effects on some fabrics than on others depending on the nature of the construction of the fabric and the magnitude of its effect on the hand in relation to the magnitude of the effect on the hand induced by the finishing agent. In addition, the relative effects of different finishing agents quite frequently vary when applied to fabrics made of different kinds of fibers. These facts make it clear that the selection of a finishing agent should be based upon the results of measurements on the same type and construction of fabric to which the agents are to be eventually applied.

The processing of fabrics involves a series of operations, each one of which may have an effect on the hand of the finished fabric. An easily made study of the effect of the different operations on the pliability of a fabric would lead to more accurate control of the operations resulting in the production or reproduction of more uniformly finished fabrics. For this purpose an instrument such as the Planoflex that gives dependable results with a minimum of effort in a very short period of time would be desirable.

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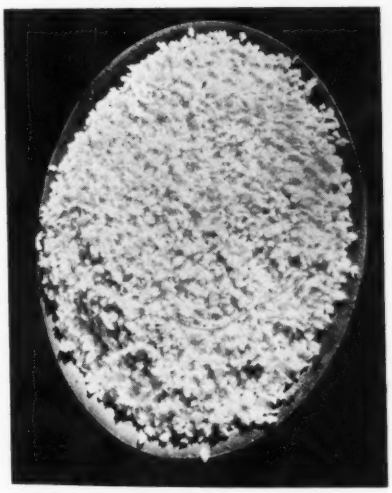
• ARALAC

After four years' experimentation, National Dairy Products Corporation recently announced successful processing of a new textile fibers for which cow's milk is the raw material.

Subjected to exhaustive tests, including resiliency, tensile strength, abrasion, odor, affinity to dyes and ability to withstand dry cleaning and washing, it is stated that the new fiber has been accepted in the textile industry and is being used in the manufacture of various kinds of fabrics.

The fiber, made from casein, a by-product of skim milk, can be blended with wool, mohair, cotton, rayon or fur in varying proportions.

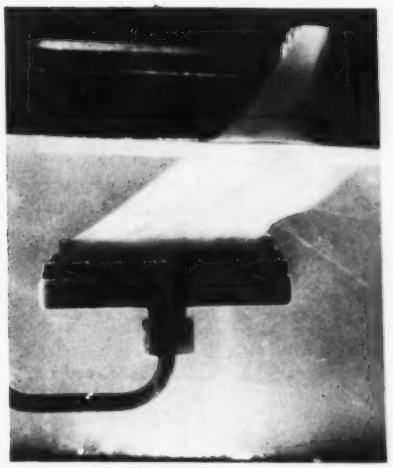


ABOVE—Shown here are curds which have been washed and dried into a rice-like substance called dried casein.

The new material—a protein fiber of the prolon family—which National Dairy calls "Aralac," imparts distinctive characteristics to fabrics in which it is used. It is more expensive than rayon and cotton; less costly than fur and wool.

Heated and treated with acids, skim milk is separated into curds and whey. The curds (casein) can be seen at the bottom.

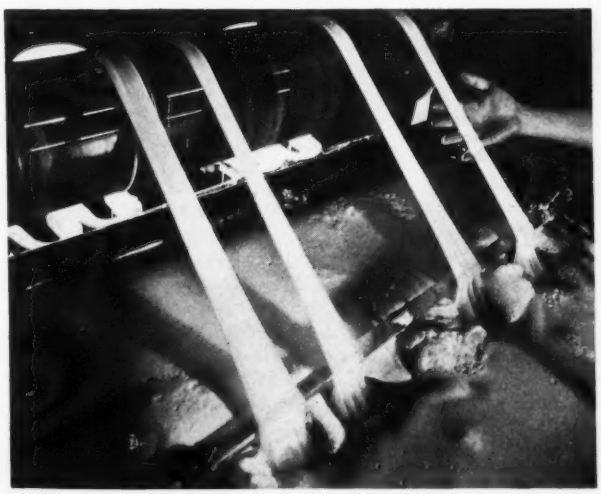
"Aralac" supplies drape and substance which previously could be obtained only through the use of fur and wool in some fabrics. Blended with rayon, it is said to produce fabrics of unusual beauty.



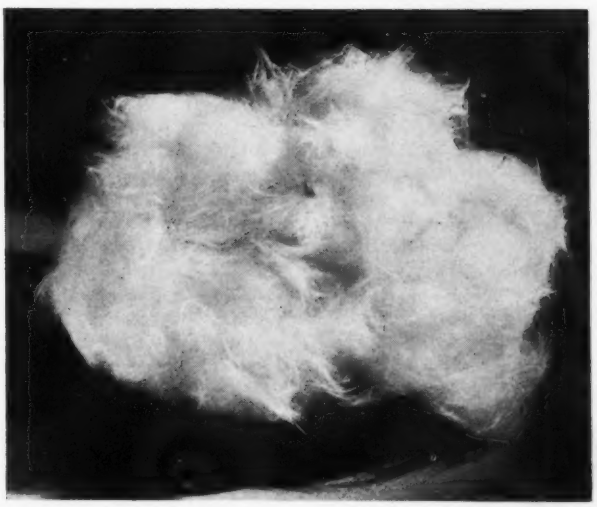
This unretouched photograph depicts a spinneret through which viscous casein is converted into fiber. To show the fiber at the exact moment when it emerges from the spinneret, the operation was simulated in a glass-enclosed case, using a chemical solution more transparent than that in which the spinneret normally is immersed.

The fiber is made at Taftville, Conn., by Aralac, Inc., a special manufacturing division established by National Dairy for that purpose. Present production capacity is about 5,000,000 pounds a year—the recoverable casein content of about 160,000,000 pounds of skim milk. The factory has been operating on a 24-hour basis for about four months, following more than two

BELOW—Four spinnerets in the spinning box are concealed in the foamy mass. In the four "tapes" are thousands of strands of fiber.



Finished "Aralac" fiber cut into small lengths and ready for blending with other fibers. It is stated that it can be cut into virtually any length—from a half-inch to a half-mile.



years' pilot plant operation at Bristol, R. I.

Much of the credit for "Aralac" goes to Atlantic Research Associates, Inc., Newtonville, Mass., a scientific research division of National Dairy. In recognition, the initials of that organization were used to form the first syllable in the name of the fiber.

Processing of fiber from milk is not new. As far back as late in the last century—even before rayon was developed—scientists were experimenting with casein fiber. National Dairy began investigating the possibility of producing a high-grade fiber from casein in 1937. Atlantic Research Associates, which was instrumental in the modern development of casein paste paint, were commissioned to experiment with casein fiber. Under the direction of Francis Clark Atwood, a noted chemist and president of ARA, who had previously conducted research for some years on casein fiber, a staff of scientists and technicians worked for months in the laboratory before they were ready for even experimental manufacture. They investigated all previous attempts to make satisfactory fiber out of casein and finally succeeded in overcoming what hitherto appeared to be insurmountable obstacles. Sheffield By-Products Company cooperated by providing improved casein.

The felt hat industry was the first to use "Aralac." Confronted with scarcity of foreign rabbit and hare fur and rising prices, fur-felt manufacturers conducted many experiments in quest of a satisfactory replacement. "Aralac" eventually was accepted. In 1940, many fur-felt hats contained the milk-derived fiber; today most fur-felt and wool felt hats in the United States, Canada and South America are made in part from cow's milk.

Textile mills also had been experimenting with "Aralac," but several processing changes were necessary before desirable blending qualities with other fibers were achieved. While the fiber was basically the same as for hats, certain adjustments had to be made in the finishing. After the processing for textiles had been perfected, the casein product was found to possess characteristics which, in some instances, resulted in fabric improvement.

Casein constitutes about 3 per cent of skim milk. After being extracted from milk, dried and ground, it is treated with chemicals and heated into a viscous, honey-like form. Forced through spinnerets under hydrostatic pressure, the emulsion emerges as thousands of strands of fiber, called "wet tow." After many other treatments, it becomes soft and luxurious. It can be cut into almost any desired length—from a half-inch to a half-mile.

• NEW DU PONT CHEMICALS

Two new industrial chemicals—sulfamic acid and ammonium sulfamate—costly laboratory curiosities three years ago with few known practical uses, are now in tonnage production at Du Pont's recently completed Grasselli, New Jersey, plant from which rising commercial demands will be met with a price reduction announced recently ranging up to 50 per cent.

Formerly produced on pilot plant scale, sulfamic acid and ammonium sulfamate proved themselves valuable in many industrial processes. An interesting application of the latter chemical has been in its wide adoption as a fire retardant in textiles, insulation products and paper. While flammable material treated with ammonium sulfamate will char upon contact with flame, it is stated that it will not blaze. Thus the treated material will not support fire.

Clothing, curtains and draperies are being "flame-proofed" with ammonium sulfamate by many laundries and dry-cleaning houses, while workers' uniforms in plants where fire-hazard is high are being protected on an increasing scale, the manufacturers point out.

Ammonium sulfamate, though harmless to humans, has proved itself highly effective in killing weed pests such as poison ivy, ragweed and thistle, without injuring the soil.

Sulfamic acid is valuable in leather tanning, for nitrite removal in the manufacture of dyes and color lakes, and also as a laboratory reagent.

Chemists explain that sulfamic acid utilized in the bating, pickling and tanning processes of leather results in a silkier and tighter grain. This white crystalline solid is odorless, highly soluble in water, non-volatile and non-hygroscopic.

In announcing the price reduction coincidental with commercial output, Du Pont also makes available samples and technical assistance.

• AQUADYE PRINTING METHOD

Aquadye printing, a new method of textile coloring employing an organic medium for use with soluble dyes is announced by the Aridye Corporation, Fair Lawn, N. J. The Aquadye method is said to make it possible to obtain with dyes many of the advantages characteristic of pigment printing colors.

The Aquadye technique is described as a further development of the original Aridye principle. It is said to bring to dyestuff printing the sharpness of mark, levelness of blotches, fine tonal gradations, and extreme detail of Aridye printing.

Deep-shade blotches, not recommended for reproduction with Aridye, may be reproduced by the Aquadye method. Aquadye can be used in combination with Aridye printing as the two mediums are compatible. No washing is required except where necessary to develop the color.

Aridye Corporation is licensing finishers under its patents which cover both the product and the process. The Aquadye pastes are solutions of synthetic binders bodied to printing consistency by emulsification with water in which the dyes are dissolved.

The method permits the finisher to use his regular dyes, but in a form which is said to improve stability, ease of running, uniformity, and soundness of mark. Aquadye is being used to print on both cotton and rayon, by machine and by screen. It is stated that experimental runs have shown the method suitable for use with direct and acid dyes, with alizarines, and with most water soluble dyes.

The Aquadye formulations can be varied to meet specific requirements for each type of dye.

The method is said to reduce preparatory work and aftertreatment to a minimum. Flannelette can be printed without renapping. Tinted grounds which will not stand washing may be overprinted by the Aquadye method. Where goods are washed, experience has indicated less let-down and a greatly reduced tendency to stain the ground, resulting in "whiter" white areas on Aquadye prints.

Dark blotches may be overprinted with Aquadye on pastel ground to produce the effect of discharge printing.

Another production advantage claimed for the Aquadye technique is the fact that the colors readily wash out of engravings, color boxes, tubs, and screens when a stream of water is applied. The new system also makes possible the use of shallower engravings.

• FIREPROOF TENTS

A recent purchase of some 214,000 Pyramidal Tents by the Quartermaster Corps introduced a new color and finish which will be utilized in all future procurements of heavy tentage, the War Department announced recently. The bright khaki color formerly used has been replaced by a dark olive drab color which is much less conspicuous to observation, particularly from the air. The new finish is said to provide the highly desirable features of fire and mildew resistance, and opaqueness to light, in addition to water repellancy.

Use of the new finishing compound has made possible the use of lighter weight 12.29 oz. per square yard (10.24 oz. per linear yard, 30" grey width) duck instead of the old standard 15.5 oz. duck, although the fire resistant treatment brings the total weight of a tent back to approximately the same weight as the old type tent in khaki dyed finish.

Action has been initiated to effect the recoloring of khaki colored heavy tentage now in use and in current stocks to provide for the more desirable dark olive

drab color. It is stated that application of the compound on old tentage also imparts opaqueness to light and mildew resistant qualities, in addition to re-waterproofing, but does not provide the fire resistant feature.

Shelter tent halves have been purchased previously in olive drab color. This same color will be continued in use for 629,000 of these tents just purchased and for future procurements. One shelter tent half is carried by each soldier, and two soldiers by erecting their halves together are provided a shelter for use in the field.

• WOOL FABRIC SPECIFICATIONS

In view of the many conflicting statements appearing in the public press regarding the use of substitutes in wool fabrics for the manufacture of uniforms for the Army, the War Department recently announced that no change is contemplated in the present specifications for these fabrics at this time.

The Quartermaster Corps, however, through its Research and Development Laboratory at the Philadelphia Depot, is conducting experiments wherein cloth containing various percentages of rayon with reworked wool is being tested. Sample pieces will be purchased in the near future for laboratory tests and for a practical test in the field.

Only in the event of a wool shortage is it contemplated changing current specifications for uniform woolen cloth.

Substitute specifications have been prepared and are continuously being revised on all items containing material which is or may become critical.

• TEXTILE FINISHING CONSULTANT

The appointment of George H. Lanier as Textile Finishing Consultant in the Textile, Clothing and Equipage Branch, Division of Purchases, OPM, was announced by Robert R. Guthrie, Assistant Director of Purchases. Mr. Lanier is a graduate of Washington Lee University, and also attended the Philadelphia Textile School. He has been associated with the J. B. Warne, Inc., of New York City, as vice-president, for the past eleven years.

• A.S.T.M. STANDARDS

In addition to all of the 68 specifications, tolerances, tests and definitions pertaining to textile materials this 400-page publication sponsored by the American Society for Testing Materials' Committee D-13 gives a great deal of other pertinent information, including extended abstracts of four technical papers covering synthetic textile fibers, merit of three rayon taffetas in consumer service, testing breaking strength of fabrics by the pendulum and inclined plane machine, and a correlation between laboratory abrasion tests and service life of men's and women's outerwear.

Other appendices aggregating about 60 pages include extensive photomicrographs of common textile fibers, yarn number conversion table, psychrometric table for relative humidity, and a glossary of terms relating to textile materials with two supplements, one covering defects in woven fabrics (definitions and photographs), the other giving terms relating to hand of fabrics.

Also given are five proposed standards published for information. They cover methods of test for accelerated aging of textiles, quantitative determination of Tussah silk in mixtures with other fibers, quantitative analysis of textiles composed of wool and lanital, and for identification of finishes on textiles.

The specifications and tests are arranged in six main groups: five standards applying to asbestos, 23 to cotton, four are relatively new methods covering glass textile products, 10 pertain to rayon, silk, and jute, and 12 cover widely used wool products. A general group includes requirements for various tests such as fastness to light, fire-retardant properties, resistance to water, methods of identifying fibers, quantitative analysis and other generally applicable specifications and tests.

Copies of this publication which includes an index to methods of test can be procured from A.S.T.M. Headquarters, 260 S. Broad St., Philadelphia, Pa., at $2.00 each; in lots of 10 to 49, $1.50 each.

• DEFENSE HANDBOOKS

Two important defense handbooks, one summarizing all price and priority regulations to date and the other listing every product subject to export control, have just been published by the N. Y. Journal of Commerce.

All government and voluntary price controls and priorities are brought up to date in the Price and Priority Digest. In addition to giving the status of nearly 200 commodities and commodity groups, prospects for civilian allotments are also reviewed for quick reference on part of the purchasing executive.

The new edition of the Export Control List embraces 32 pages of product listings with all licensing and destination symbols posted next to each item. It is the fifth revision of this export guide.

Both supplements have been published in handy tabloid form and may be had at 10 cents each from the N. Y. Journal of Commerce, 63 Park Row, New York. A limited supply of O.P.M. and O.P.A. order texts, as published in the columns of the Journal of Commerce, is also available at the same price.

• GENERAL RELEASE

General Dyestuff Corp., 435 Hudson Street, New York City, has recently released a circular describing the following product:

Naphtol AS-KR Supra—a new addition to General's Naphtol AS line. With the various Fast Color Salts and Bases, it produces a large variety of shades, many of which are dischargeable. Among the shades produced are: a bright orange with Fast Orange Salt GCS, a burnt orange with Fast Red Salt AL, a bright scarlet with Fast Scarlet Salt RN, and a deep red with Fast Red Salt 3GL. It is of low substantivity and is well suited for padding. Being a Supra brand, this new Naphtol is a dispersed type, and solutions, particularly for padding, can be prepared by adding the Naphtol to a boiling alkaline water solution. Circular G-291.

• KNITTING ARTS EXHIBITION

At a meeting of the board of directors of the National Association of Hosiery Manufacturers on October 23rd, it was voted that the Knitting Arts Exhibition be changed from an annual to a biennial event, starting in 1942, and that it be held in Atlantic City instead of Philadelphia. A survey of exhibitors made by the association indicated an overwhelming preference for the change.

• WORSTED-TYPE RAYON YARNS

Installation of new equipment for experimental production of worsted-type yarns from rayon staple fiber and rayon blended with wool and other fibers has just been completed by the American Viscose Corporation at its Textile Unit at Marcus Hook, Pa. The equipment will be used exclusively for experimental work to test rayon products, to improve methods of manufacture, and to develop additional uses of rayon staple fiber in worsted-type fabrics. Many blended fabrics of this type are already well established in the market for women's wear and men's wear, including summer suitings. It is expected that the new equipment will be used extensively to help individual textile firms in the solution of problems arising in the manufacture of worsted-type fabrics from rayon staple fiber and to help such firms to develop new or improved fabrics.

The Textile Unit was established in 1940, as a major part of the American Viscose Corporation's research and development program. It is a separate and self-contained research plant containing a wide variety of types of equipment used in every phase of textile production, including warping, weaving, knitting, dyeing and finishing, besides cotton spinning and the newly added worsted spinning machinery. It is devoted exclusively to experimental production and has five principal objectives: (1) to estab-

lish high quality standards for the company's products; (2) to develop better production equipment and methods for fabrics containing the various types of rayon yarn and staple fiber; (3) to aid the textile industry in the development of new fabrics; (4) to perfect new types of rayon yarn and staple fiber; and (5) to afford educational facilities for members of the company's staff.

The newly installed worsted equipment consists of a standard Bradford drawing and spinning layout which handles the manufacture of worsted spun yarns from the top of the spun yarn. The preliminary processes of carding, combing, and gilling necessary to produce top, are now being installed and are expected to be in full operation within a few weeks. When this installation is completed the rayon staple fiber can be processed through all manufacturing operations from the bale to the finished yarn, and in connection with other facilities of the Textile Unit can be woven and finished in the standard 54-inch width fabric common to the worsted industry.

Like other sections of the company's Textile Unit the Worsted section is partitioned off in such a manner as to provide separate humidity and air temperature control. This flexibility makes it possible to study the effects of various degrees of temperature and humidity and in fact duplicate manufacturing conditions existing in the worsted industry. In this way ideal operating conditions can be determined as well as what changes in operating procedures are necessary to conform with conditions as they exist in customer's plants.

• PERKIN MEDAL AWARD

Dr. Martin H. Ittner has been elected to receive the Perkin Medal of the Society of Chemical Industry for 1942. The medal is awarded annually for outstanding work in applied chemistry, and the medallist is selected by a committee representing the five chemical societies in the United States.

Dr. Ittner was born in Berlin Heights, Ohio, on May 2, 1870. He received a B.A. degree from Washington University in 1892, and after two years' additional work there received a B.S. degree. In 1895 he received an M.A. degree and in 1896 a Ph.D. degree from Harvard Graduate School. In 1930 Colgate University conferred on him an honorary Ph.D. degree and in 1936 he received an L.L.D. from Washington University.

For almost 45 years Dr. Ittner has been in charge of research at Colgate-Palmolive-Peet Company or predecessor companies. Among Dr. Ittner's many contributions is his development of a successful commercial process for the hydrogenation of fatty oils, on which process he has been granted a number of patents. He has also made valuable contributions in the field of distillation and he holds several recent patents pertaining to new processes for glycerine production.

The medal will be presented on January 9, 1942, at a meeting to be held at The Chemists' Club, 52 East 41st Street, New York City. Details of this meeting will be announced at a later date.

• HYGIENIZED PROCESS

The "Hygienized Process" has been taken over by the Quaker Chemical Products Corporation of Conshohocken, Pa. A separate "Hygienized Division" had been set up under the management of Larry J. Margulies, who is a pioneer in the development of hygienic processing of textiles.

It is stated that a fabric that has been "Hygienized" has, in effect, been given a sanitary process which renders it actively antiseptic, as defined in United States Department of Agriculture's Bulletin No. 198. This means that the fabric is bacteriostatic and fungostatic, thus retarding germ growth and resisting perspiration odors that form in wearing apparel, bed wear or any material.

The "Hygienized Process" is being applied to all wearing apparel, mattresses, pillows, bedwear, household textiles, hosiery, shoes and children's wear. The "Hygienizing Compounds" are applied in with the regular finishing materials used in the trade, and are applied without any additional operations.

A separate New York office for this Division has been established at 1441 Broadway.

• CLASSIFIED ADVERTISEMENTS •

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

WANTED: Manufacturing Chemist, excellent opportunity, to take charge of production and laboratory. Broad experience in textile scouring, dyeing and finishing compounds—including gums, starches, resins, pigments, soaps, etc. Jersey City vicinity. Write Box No. 349, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

WANTED: Analytical Chemist to work in laboratory of textile finishing plant in Southern New England. State age, education, experience, draft status and salary expected. Write Box No. 352, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

POSITION WANTED: Yarn dyer, 14 years' experience on Cotton, Rayon and Silk skeins and packages. Capable of taking full charge of dyehouse. Always held responsible position, desires to locate in New England. Best of references. Write Box No. 353, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

WANTED: Capable piece dyer experienced on Vat production, Khaki Olive Drabs and other Vat shades. Perfect shade matching required. In reply furnish full details first letter as to experience, salary expected, etc. Write Box No. 354, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

Use Reporter Classified Advertisements for Results!